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The use of bioremediation processes to treat hazardous waste has increased in the last 10 years. Biological treatment offers the advantage of contaminant destruction rather than transfer to other media. There is concern, however, that significant amounts of organic pollutants are emitted to the air from biological treatment activities before they can be degraded. To estimate the magnitude of emissions from these facilities, overall fate models that incorporate the effects of several competing removal mechanisms are needed.

This report focuses on the state-of-the-art in modeling air emissions from bioremediation processes. The biological treatment systems are described, as are the important pathways that affect the fate of organic pollutants in those systems. Currently available models are identified, described, and evaluated for each bioremediation process. Finally, some limitations of the models and the need for additional research are discussed.

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AVAILABLE MODELS FOR ESTIMATING EMISSIONS RESULTING FROM BIOREMEDIATION PROCESSES-- A REVIEW

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FOREWORD

As environmental controls become more costly to implement and the penalties of judgment errors become more severe, environmental quality management requires more efficient analytical tools based on greater knowledge of the environmental phenomena to be managed. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Assessment Branch develops and evaluates management or engineering tools to help pollution control officials address environmental problems.

Biological treatment systems offer the potential for reducing or eliminating human health risks resulting from the treatment-disposal of hazardous wastes. Atmospheric emission of organic compounds may occur, however, before or during biotreatment, and mathematical models are available to estimate the extent to which volatilization occurs at these facilities. This report reviews the state-of-the-art in methods and models for estimating emissions from bioremediation processes, with emphasis on techniques that incorporate the competing effects of biological activity, volatilization, and other mechanisms on the fate of organic pollutants.

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ABSTRACT

The use of bioremediation processes to treat hazardous waste has increased in the last ten years. Biological treatment offers the advantage of contaminant destruction rather than transfer to other media. However, there is concern that significant amounts of organic pollutants are emitted to the air from biological treatment facilities before they can be degraded. In order to estimate the magnitude of emissions from these facilities, overall fate models that incorporate the effects of several competing removal mechanisms are needed.

This report focuses on the state-of-the-art in modeling emissions from bioremediation processes. The biological treatment systems are described, as are the important pathways that affect the fate of organic pollutants in those systems. Currently available models are identified, described, and evaluated for each bioremediation process. Finally, some limitations of the models and the need for further research are discussed.

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SECTION 1

INTRODUCTION

1.1 BACKGROUND AND OBJECTIVES

As part of its Superfund support activities, the EPA Office of Research and Development has formed the Biosystems Technology Development (BTD) Program to investigate new biological treatment systems. These systems may provide the potential to reduce or eliminate the human health risks associated with the treatment and/or disposal of hazardous wastes. As part of its mandate, the BTD Program identifies, evaluates, and develops information on the efficacy and applicability of biological treatment systems for use in assessing appropriate remediation alternatives.

Biological treatment of organic pollutants offers the advantage of contaminant destruction rather than transfer to other media. However, concern has grown in recent years that many volatile organic pollutants are emitted to the atmosphere from biotreatment facilities before they can be degraded. Shen and Sewell (1988) provide estimates of emissions of volatile organic compounds (VOCs) from hazardous waste treatment, storage, and disposal facilities (TSDF) that suggest that concern is justified (see Table 1-1). In response to the increased attention, a number of models have been developed that predict the fate of organic pollutants during specific bioremediation processes.

This report focuses on the potential for bioremediation processes to transfer contaminants between the soil or water and the air. The intent is to identify, describe, and evaluate available methods and models for estimating atmospheric emissions from bioremediation processes used to treat hazardous waste. Models that consider only volatilization will tend to overpredict the magnitude of air emissions from bioremediation processes. Therefore, this report concentrates on models that incorporate the competing effects of biological activity, volatilization, and possibly other mechanisms, such as adsorption and transport, on the fate of organic pollutants. Models of some non-biological components of the treatment processes also are included.

1.2 CONTENTS OF THE REPORT

This report is divided into ten sections. Section 2 describes the important pathways by which pollutants are transferred from a waste treatment site. Generally accepted theories associated with each pathway are briefly summarized. In addition, when possible, methods of estimating equilibrium and rate constants are presented. These constants are needed to apply the models described in later sections.

TABLE 1-1. COMPONENTS OF EMISSIONS OF 54 SELECTED VOCS FROM TSDF ACTIVITIES (from Shen and Sewell, 1988)

Component	Amount (metric ton/yr)
Treatments tanks	530,000
Nonaerated surface impoundments	796,000
Storage	420,000
Treatment	310,000
Disposal	66,000
Aerated surface impoundment	66,000
Landfills	190,000
Land treatment and applications	43,000
Storage tanks	10,000
Total of components	1,635,000

In Section 3, bioremediation processes that are currently in use or in advanced stages of research are presented. Each process is briefly described in terms of its operation and component parts, the types of contaminants treated, advantages and disadvantages associated with its use, and the likelihood of air emissions.

An extensive literature search was conducted to locate models that simulate the fate of organic pollutants for each biotreatment process. Sections 4 through 7 contain summaries of the models located during that search. Models are summarized in terms of their theoretical basis, assumptions, and the mechanisms of transport and fate that are considered. Input requirements, output, previous model applications, resource requirements, ease of use, and model availability also are discussed briefly. Air emissions from some biotreatment processes have not been modeled. For those processes, the current status of research is discussed. Section 8 briefly presents the status of modeling two physical remedial processes often used in conjunction with bioremediation efforts.

Current efforts to model the fate of hazardous compounds at biological treatment facilities suffer from a number of limitations that should be understood by users of the models described in this report. These limitations and the related need for further research are discussed in Section 9.

Section 10, the bibliography, lists relevant references, grouped according to subject. The groups of references are listed in approximately the same order as they are discussed in the text. References on a particular subject can be located quickly by referring to the Table of Contents.

A large number of equations, some of which are very complex, have been reproduced in this report. Although the equations have been checked carefully for accuracy, it is strongly recommended that the user refer to the original publication before applying any model. Occasionally, errors occur in the original reference. When detected, the errors are noted in the model summaries of this report.

1.3 SUMMARY OF CONCLUSIONS AND RESEARCH NEEDS

Conclusions drawn from this report are:

1) Models of bioremediation processes are empirical. Data are unknown or incomplete and the interrelationships of components and pathways are complex. Moreover, at wastewater treatment facilities, the concentrations of hazardous organics can vary by several orders of magnitude on a daily basis. Thus, the release of organics to the air or other media from bioremediation sites is difficult to estimate.

2) There is a correlation between operational experience with a biotreatment process and the state-of-the-art in modeling that process. No models exist for some innovative new processes. For some wastewater treatment processes, only models of substrate removal exist. On the other hand, many models have been developed to describe the fate of pollutants in some commonly used treatment processes. Most of the models identified for this project are analytical models based on a mass-balance approach. Some more complex numerical models also are reviewed.

3) Among the suspended-growth systems, a number of models have been developed to describe activated-sludge aeration tanks and surface impoundments. Biodegradation, adsorption, and volatilization and/or stripping are the removal mechanisms considered. Most of the models describe steady-state, completely-mixed conditions. Few models of sequencing batch reactors or of powdered activated carbon treatment are available.

4) No models have been produced to simulate the emission of organic pollutants from fixed-film biological treatment systems. Most available models reflect a concern for substrate removal, in terms of biological oxygen demand (BOD). Under some conditions, estimates or measurements related to the mass transfer of oxygen can be used to approximate air emissions from these systems.

5) Among soil-incorporation systems, land treatment facilities have been modeled most. The fate mechanisms included in the models include biodegradation, diffusion and volatilization, adsorption, and solute transport. The models are non-steady-state and output is generated for specified times. No mathematical models exist to describe the composting of hazardous materials. One model simulates biodegradation of organic vapors in a soil treatment bed.

6) A number of models predict the fate of organic pollutants in the subsurface under natural conditions. The unsaturated-zone models are not designed to simulate in-situ bioremediation, which often

includes air sparging to stimulate microbial growth. While some of the saturated-zone models can be applied to in-situ bioremedial efforts, they can not be used to directly estimate air emissions. Pollutant vapors escaping from a contaminated aquifer must pass through the unsaturated zone. Thus, the likelihood and magnitude of air emissions from the saturated zone must be modeled using an unsaturated zone model with a pollutant source term supplied at the water table boundary.

7) The biodegradation of organics in biological treatment facilities is poorly understood and limited data are available to estimate the biodegradation rate constants for compounds of interest. In addition, data generated in laboratories may vary greatly from field study data. Thus, reported values should be used with caution and experimentally verified when possible.

8) Suspended-growth system modeling results have been shown to be very sensitive to the values of the biodegradation parameters (U.S. EPA, 1987b). Thus, when accurate information about biological activity is not available, modeling studies should use a range of values, including zero, for the biodegradation rate constant. By ignoring biodegradation, estimates of air emissions under "worst-case" conditions (e.g., periods of acclimation or of inactivity due to toxic shock) are obtained.

9) Most of the models summarized in this report have not been validated in the field. When predicted model results are compared to laboratory or field data, many authors report agreement within an order-of-magnitude. That level of agreement is generally considered adequate for screening purposes. Because of the many assumptions incorporated into the models, they should be used with caution for detailed site-specific studies.

10) To be able to adequately predict air emissions from biological treatment facilities, further research is needed in several areas. More collection of field data is needed, both in order to understand the severity of the problem and in order to aid in model development and validation. An improved understanding of the kinetics of biodegradation in multi-component heterogeneous systems is needed. For some processes, first-generation fate models have yet to be developed. For other processes, the capabilities of the current models could be expanded.

SECTION 2[**]

DESCRIPTION OF PATHWAYS FOR TRANSFER OF CONTAMINANTS FROM HAZARDOUS WASTE TREATMENT SITES

This section discusses the general pathways for transfer of contaminants from a hazardous waste site, and the significance of these pathways for removing volatile organics from biological treatment facilities.

2.1 INTRODUCTION

In this report, a pathway is defined as a process whereby contaminants, and specifically volatile organics, can be removed from a site. Only sites which use biological treatment processes will be considered here. These processes include suspended growth systems, such as activated sludge and surface impoundments, fixed-film systems, soil incorporation systems, such as landfarming, and in-situ bioremediation processes. The significance of the different pathways for removal of organic chemicals is dependent on the type of treatment facility, and the operational procedures at the facility.

In hazardous waste treatment, storage and disposal facilities (TSDF), contaminants may escape from a site by one or more pathways, such as volatilization, biodegradation or photochemical decomposition, and enter another compartment of the environment. The pathways used, and the rates of removal of the contaminant depend on a wide variety of factors, some of which are easily quantified, and others which are far more difficult to determine. However, it is often necessary to obtain some understanding of the predominant pathways by which a volatile organic is being removed from a site, and to estimate the rates of removal. The potential pathways by which volatile organics could depart from a hazardous waste site, the processes involved in each of these pathways, and the probable significance of the pathway for biological treatment facilities are discussed below.

The pathways considered below are predominantly those discussed in the 1987 U.S. EPA report entitled Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF)--Air Emission Models (U.S. EPA, 1987b).

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2.2 VOLATILIZATION AND STRIPPING AT AN AIR-WATER INTERFACE

2.2.1 Volatilization Process

Volatilization is the process of vaporization of contaminants, such as volatile organics, from water or soil to the atmosphere. For quiescent liquids, the driving force for volatilization is molecular diffusion, caused by differences in chemical potential (concentration) of the contaminant between the two media (U.S. EPA, 1987b). Rates of volatilization from water depend on solvent-solute interactions and can be estimated using measurable quantities, such as a contaminant's aqueous solubility, vapor pressure, Henry's law coefficient, and diffusivity coefficient. Volatilization rates are also a function of the characteristics of a water body such as its depth, flow rate, presence of waves, sediment content, and the presence of other compounds, as well as the atmospheric conditions above the water body, including the wind speed and stability (Lyman et al., 1982).

2.2.2 Mass Transfer Models

The rate of volatilization is essentially the rate of mass transfer from the water, across the air/water interface and into the atmosphere. Several theories have been proposed which describe mass transfer between fluid phases such as air and water. The most widely-used model is the two-film theory, first proposed by Liss and Slater (1974) and later extended by Mackay and others (1975; 1977; 1979). Recently, several other mass transfer models have been proposed, including the penetration theory, surface renewal theory and film penetration theory, which are discussed briefly below. However, all of the models discussed in this report use either the two-film concept or simply assume that equilibrium conditions exist when estimating the flux of contaminants across the air/water interface.

2.2.2.1 Two-Film Model--

In the two-film model, the compound is transported from the bulk of one phase to the phase boundary, and then from the interface to the bulk of the second phase. The main bodies of the liquid and the gas phases are assumed to be well-mixed, with constant concentrations of C_L and C_G. Near the air/water interface, there is a concentration gradient in both the liquid and the gas phases. At the interface there is a discontinuity of concentration, and the ratio of the air and water concentrations is assumed to equal Henry's law constant, which is discussed below. Figure 2.1 shows the relationship between the concentrations according to the two-film theory. Transfer through the two films is by molecular diffusion, which is expressed by a diffusion coefficient, D. The rate of mass transfer is proportional to the diffusion coefficient, the interfacial area across which transport occurs, the concentration gradient at the interface, and the film thickness, δ. Transport to the interface through the liquid can be written, using Fick's first law, as (Roberts et al., 1984):

$$-\frac{dm}{dt} = D\,A\,\frac{\partial C}{\partial x} = A\,\frac{D_L}{\delta_L}\,(C_L - C_{int,L}) \qquad (1)$$

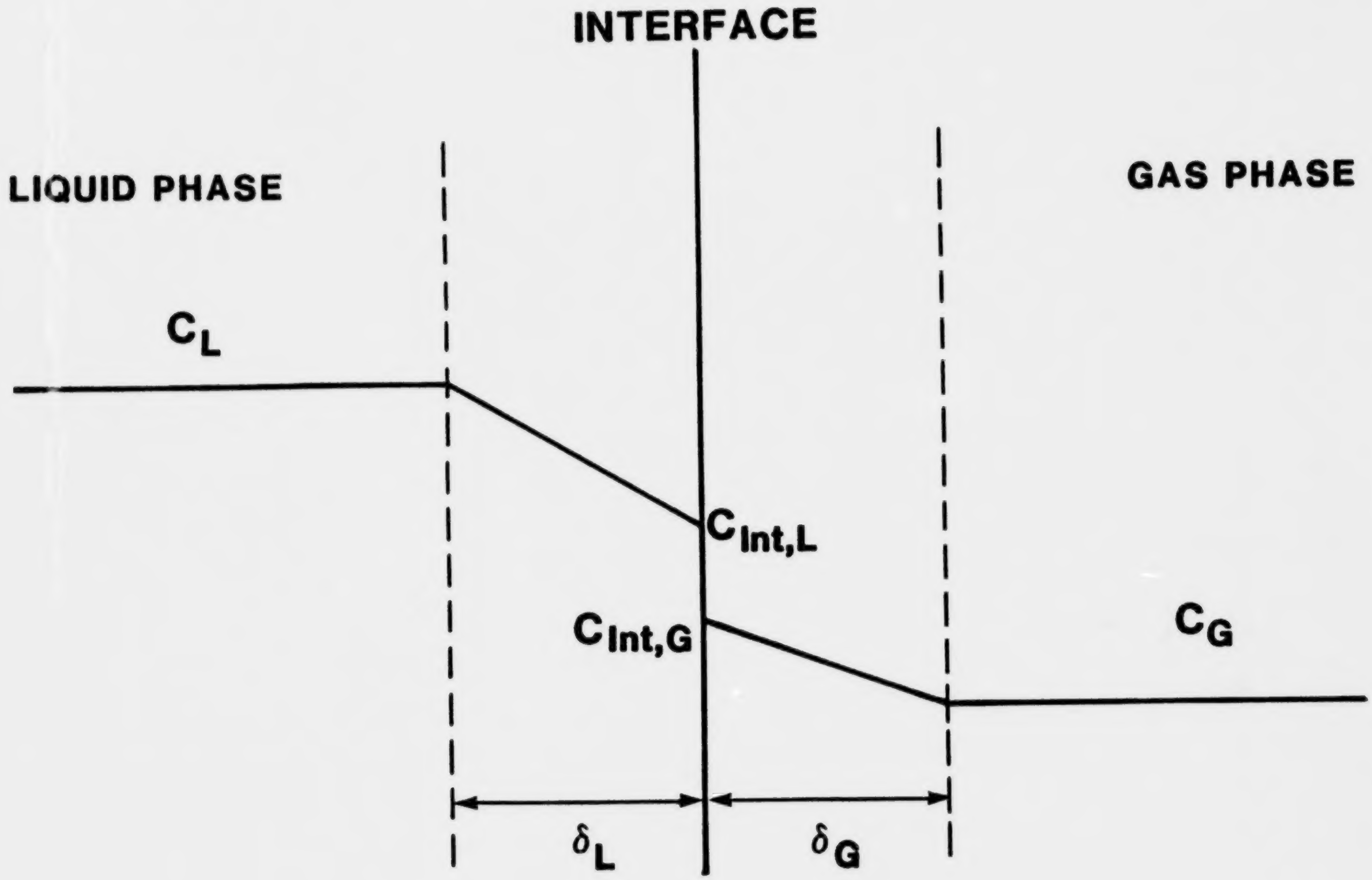
INTERFACE
LIQUID PHASE
GAS PHASE
C_L
$C_{Int,L}$
$C_{Int,G}$
C_G
δ_L
δ_G

Figure 2.1. Concentration profile based on the two-film theory (from Roberts et al., 1984).

and the mass transport from the interface through the gas can be written:

$$-\frac{dm}{dt} = D\ A\ \frac{\partial C}{\partial x} = A\ \frac{D_G}{\delta_G}\ (C_G - C_{int,G}) \qquad (2)$$

where

D = diffusion coefficient (m^2/s)

D_L = diffusion coefficient in the liquid phase(m^2/s)

δ_L = film thickness in the liquid phase (m)

D_G = diffusion coefficient in the gas phase (m^2/s)

δ_G = film thickness in the gas phase (m)

m = mass (g)

A = interfacial area (m^2)

$C_{int,L}$= concentration at interface in liquid (g/m^3)

$C_{int,G}$= concentration at interface in gas (g/m^3)

C_L = concentration in liquid phase at edge of film (g/m^3)

C_G = concentration in gas phase at edge of film (g/m^3)

The ratio D/δ is known as the mass transfer coefficient. Therefore, the liquid-film mass transfer coefficient, k_L, can be written:

$$k_L = \frac{D_L}{\delta_L} \quad (m/s) \qquad (3)$$

and the gas-film mass transfer coefficient is written:

$$k_G = \frac{D_G}{\delta_G} \quad (m/s) \qquad (4)$$

In actual applications of these equations, the concentrations in the bulk of the gas and liquid phases, C_G and C_L, are easily measured, whereas the determination of $C_{int,G}$ and $C_{int,L}$ is nearly impossible. Therefore, overall mass transfer coefficients, K_G and K_L, can be defined using the following relations:

$$-\frac{dm}{dt} = K_G\ A(C_G^* - C_G) \qquad (5)$$

$$-\frac{dm}{dt} = K_L\ A(C_L - C_L{}^*) \quad (6)$$

where

$C_G{}^*$ = gas phase concentration in equilibrium with the liquid (g/m^3)

$C_L{}^*$ = liquid phase concentration corresponding to an equilibrium condition with the gas (g/m^3)

These new variables may be related to the concentrations, C_L and C_G, by (Roberts et al., 1984):

$$C_G{}^* = C_L(H_c) \quad \text{and} \quad C_L{}^* = C_G/(H_c) \quad (7)$$

where

H_c = non-dimensional Henry's constant

Henry's law constant describes the ratio of the concentration of the compound in the gas to the concentration in the liquid at equilibrium, for dilute aqueous solutions and low partial pressures of the gas. This relationship can be written:

$$H_c = \frac{C_{int,G}}{C_{int,L}} \quad (8)$$

In many applications, the concentration of a contaminant in the gas phase above the liquid can be considered negligible. This would occur, for example, if there was a wind which transported the contaminant away from the air/water interface at a rapid enough rate that no layer of high concentration could develop above the water body. In this case, the concentration C_G is 0, and substituting this value into Equation 7, gives:

$$C_L{}^* = C_G/(H_c) = 0/(H_c) = 0 \quad (9)$$

and Equation 6 simplifies to:

$$-\frac{dm}{dt} = K_L\ A(C_L) \quad (10)$$

Therefore, if the assumption is made that the concentration in the gas is zero, the equation for the rate of mass transfer from the liquid to the gas simplifies to a first-order rate equation. Similar rate equations are also written for the rate of change in concentration with time. The above equation can be modified for concentration by dividing both sides by a volume term. The units of the parameters should be consistent with the form of the equation used.

Care should be taken that the units used for the parameters in the mass transfer equations are consistent with the equation to which they are applied, since there are several different units which are commonly used. In the previous discussion, the mass transfer coefficients are in units of m/s. These units can be converted to g-mol/cm^2-s, or sec^{-1} by a method presented in Hwang (1982). Furthermore, many authors consider the individual phase mass transfer coefficients multiplied by the specific surface area, a, as the overall rate constant which has units of sec^{-1}. The coefficient is written K_La, where a is in units of m^2/m^3. Both conventions will be used in this report, since the equations presented are not modified from the original sources.

The overall mass transfer coefficients for the gas phase (K_G) and for the liquid phase (K_L) can be related to the Henry's law constant and the individual liquid- and gas-phase mass transfer coefficients as follows (Roberts et al., 1984):

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H_c}{k_L} \quad \text{and} \quad \frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{H_c k_G} \tag{11}$$

The dimensional form of Henry's coefficient, H, is related to the non-dimensional form by the equation:

$$H = H_c RT = \left(\frac{C_G}{C_L}\right) RT \tag{12}$$

where

H = Henry's coefficient (atm-m^3/mol)

H_c = Henry's coefficient (dimensionless)

R = universal gas constant (atm-m^3/mol-K)

T = temperature (K)

C_L = concentration in liquid phase at edge of film (g/m^3)

C_G = concentration in gas phase at edge of film (g/m^3)

When H is substituted for H_c, the equation is in the form used by Mackay and Leinonen, (1975):

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{RT}{Hk_G} \quad \text{and} \quad \frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{RTk_L} \tag{13}$$

The relationship between the individual-phase mass transfer coefficients can be expressed by the sum of the resistances of the gas and liquid phases. The resistances of the liquid and gas phases can be expressed:

$$R_T = R_L + R_G \qquad (14)$$

where

R_L = resistance of the liquid phase = $\frac{1}{k_L}$

R_G = resistance of the gas phase = $\frac{RT}{Hk_G}$

Experimental work by Liss (1973), Schooley (1969), and Goodgame and Sherwood (1954) has shown that the concept of additivity of resistances is likely to be an accurate representation of the mass transfer system.

The ratio of the two resistances can be written:

$$\frac{R_L}{R_G} = \frac{Hk_G}{RTk_L} = \frac{H_c k_G}{k_L} \qquad (15)$$

If R_L/R_G equals one, then the resistances of the two phases are equal and both phases control the rate of mass transfer equally. Mackay and Leinonen (1975) found that this occurs when $H = 1.6 \times 10^{-4}$ atm-m^3/mol, assuming $k_G/k_L = 150$. However, Munz and Roberts (1984) suggest that a k_G/k_L ratio of 20 is more appropriate for natural water surfaces, which would affect the value for H for which the resistances of the phases are equal. For a given ratio of k_G/k_L, the Henry's Law coefficient, H, will provide information on which phase controls the rate of mass transfer, and therefore the rate of volatilization of the compound. Estimates of volatility for different ranges of Henry's law constants are presented in Mackay (1977) and Lyman et al. (1982).

2.2.2.2 Other theories of mass transfer

The penetration theory of mass transfer, first proposed by Higbie (1935), is based on the conceptualization of packets of fluid which are transported to the liquid/gas interface, remain for a short and equal amount of time, and then are displaced back into the fluid. A mass transfer equation can be developed for this process, using Fick's second law. The initial and boundary conditions are presented in Roberts et al. (1983). In this equation, the liquid-phase mass transfer coefficient, k_L, is a function of the square-root of the diffusion coefficient, D_L. This differs from the two-film model in which k_L is linearly dependent on D_L.

The penetration theory was extended by Danckwerts (1951) who proposed the surface-renewal theory. The two models are similar, except that in the surface-renewal theory, the packet of fluid at the interface may reside there for any length of time, as opposed to the constant length of time required in the penetration theory. Danckwerts introduces a parameter which is related to the probability that one packet of fluid will be replaced at the interface by another packet, and a mass transfer equation can be written incorporating this parameter (Roberts et al., 1984). In this equation, the mass transfer coefficient, k_L, is also dependent on the square-root of the diffusion coefficient, D_L.

The film-penetration theory is essentially a combination of the two-film, penetration and surface renewal models. It was presented by Toor and Marchello (1958). In this model, a laminar layer is assumed to exist at the surface, which provides all resistance to mass transfer. The two-film model is applied to the transfer through older elements of the liquid or gas, and penetration theory is used for the younger elements of the phase. The corresponding mass transfer equations are presented in Roberts et al. (1984). The film-penetration model is rarely used in practice since equations describing this model contain several parameters which are difficult to measure.

2.2.3 Estimation of Parameters Used in Liquid-Air Mass Transfer Equations

2.2.3.1 Henry's Law Coefficient--

Henry's law expresses the relationship between the solubility of a gas in water and the partial pressure of the gas in the atmosphere above the water. It is valid only for dilute solutions. The Henry's law coefficient, which represents equilibrium conditions between the liquid and gas phases, is a function of the type of gas, the compounds present in the liquid, and the temperature (Tchobanoglous and Schroeder, 1985).

Values for Henry's law coefficient are widely available. Care should be taken to apply the correct form of the constant (dimensional or non-dimensional), and units, for the equation being used. H_c can be converted to H by Equation 12. The values for Henry's constant are tabulated in Jury et al. (1984) and Schnoor et al. (1987). If the value for H for a particular compound is not available it may be estimated from:

$$H = \frac{P}{(14.7s)} \tag{16}$$

where

H = Henry's law coefficient, atm-m^3/g-mol

P = pure component vapor pressure, psia

s = solubility of chemical in water mol/m^3

14.7 = conversion factor--psia to atmospheres (U.S. EPA, 1987b)

The value of the Henry's law coefficient for a particular compound provides important insight on the tendency of the compound to volatilize, as per the following guidelines:

1. For compounds with $H < 3 \times 10^{-7}$ atm-m^3/mol, volatilization can be considered unimportant as a pathway for removal of the contaminant.

For larger values of H, the compound can be considered to be volatile (Lyman et al.,1982).

2. When $3 \times 10^{-7} < H < 2 \times 10^{-5}$ atm-m^3/mol, the compound tends to partition into the liquid, and the mass transfer rate is controlled by the gas phase.

3. For values of H between 2×10^{-5} and 2×10^{-2} atm-m^3/mol, both the liquid and the gas phases are important in controlling the mass transfer rate.

4. When $H > 2.4 \times 10^{-2}$ atm-m^3/mol, the gas phase resistance is negligible, and only the liquid phase will control the rate of mass transfer (Barton, 1984).

2.2.3.2 Raoult's Law--

In some situations commonly present at hazardous waste sites, mass transfer occurs through a surface film of oil. Three resistances acting in series control emission: from the liquid to the oil, through the oil, and from the oil to the air (U.S. EPA, 1987b). Means of estimating emissions for this complicated condition are normally not available. However, by making the simplifying assumptions that the oil layer is relatively thin, and that mass transfer is controlled by the gas-phase resistance, the mass transfer coefficient can be written (U.S. EPA, 1987b):

$$K = k_G K_{eq} \qquad (17)$$

where

K = overall mass transfer coefficient (m/s)

k_G = gas-phase mass transfer coefficient (m/s)

K_{eq} = equilibrium constant (dimensionless)

K_{eq} describes the equilibrium partitioning between the liquid and gas phases, and should be calculated using an equation expressing equilibrium conditions. Since Henry's law is valid only for dilute solutions, it is not recommended for use with concentrated mixtures of organics in a separate oil layer. Under these circumstances, Raoult's law should be used to determine the equilibrium partitioning between the liquid and gas phases (U.S. EPA, 1987b). Raoult's law relates the vapor pressure of a liquid which includes a dissolved compound, with the vapor pressure of the pure liquid without the compound. The functional relationships for partial pressure in a solution with two components is written according to Raoult's law (Denbigh, 1981):

$$P_A = X_A P^*_A \qquad (18)$$

$$P_B = X_B P^*_B$$

where

P_A = partial pressure of A (atm)

P_B = partial pressure of B (atm)

X_A = mole fraction of A

X_B = mole fraction of B

P^*_A = vapor pressure of pure A (atm)

P^*_B = vapor pressure of pure B (atm)

For mass transfer through an oil film, the equilibrium constant, K_{eq}, can be calculated through the application of the relationships of Equation 18 (EPA,1987):

$$K_{eq} = \frac{P^* \rho_a \, MW_{oil}}{P_o \rho_{oil} \, MW_a} \tag{19}$$

where

K_{eq} = equilibrium constant

P^* = vapor pressure of the volatile compound of interest (atm)

ρ_a = density of air (g/cm^3)

MW_{oil} = molecular weight of oil (g/mol)

P_o = total pressure (atm)

ρ_{oil} = density of oil (g/cm^3)

MW_a = molecular weight of air (g/mol)

2.2.3.3 Liquid and Gas Mass Transfer Coefficients--

Values of phase exchange coefficients may be available for some common compounds. However, if values are unavailable, they may be estimated by one of several methods. Some methods may be applicable only under a given set of conditions. It is suggested that estimates of k_L and k_G be obtained by more than one method, if possible, to determine that they produce similar results.

2.2.3.3.1 Liquid-phase mass transfer coefficient--The value of the liquid-phase mass transfer coefficient is dependent on the depth of the water body, d, on the diffusivity of the compound and on the wind speed, V (Lunney, 1983; Springer et al., 1984). Springer suggests that k_L is also directly related to the fetch, F, which is the linear distance travelled by the wind across the liquid surface. Springer experimentally determined values for k_L for ethyl ether, using different wind velocities and F/d ratios. He developed equations to calculate k_L for all conditions, except cases of wind speed greater than 3.25 m/sec and F/d ratios less than 14. The equations are presented in Table 2-1.

An equation developed by Mackay and Yeun (1983) and shown in Table 2-1 can be used for wind speed and F/d ratios outside the ranges covered by Springer's equations, as suggested in U.S. EPA, 1987b. The Mackay and Yeun equations are based on measurements of volatilization rates for 11 organic compounds with differing Henry's law constants. They do not include the effect of differing depths in their equations. Mackay and Yeun caution that the volatilization rate may be overestimated if there are organic or mineral sorbing solids present, since they will reduce the solute fugacity or partial pressure. Furthermore, for wind speeds > 22 m/s, the equations may not be applicable due to frequent wave breaking and spray transfer.

Southworth (1979), using laboratory data, developed a method for determining k_L and k_G for polycyclic aromatic hydrocarbons (PAHs) in turbulent water bodies, such as rivers. This method is applicable to compounds with a range of Henry's law coefficients between 10^{-5} and 10^{-3} atm-m^3/mol. This method requires a knowledge of the flow velocity, the wind velocity, the depth, and the molecular weight of the compound. The equations are presented in Table 2-1. Estimates of k_L and k_G for a variety of compounds and conditions, which were calculated using Southworth's equations, are tabled in Lyman et al. (1982).

Cohen et al. (1978) also present a method for estimating k_L, which is included in Table 2-1. They have delineated three ranges of wind speeds, V_{wind}, which affect the value of k_L. For $V_{wind} < 3$ m/s, when the water surface is calm and there is little or no turbulence, values of k_L are approximately 2-3 cm/hr. When V_{wind} is between 3 and 10 m/s, there is increased surface roughness and k_L increases from 3 to 30 cm/hr. For $V_{wind} > 10$ m/s, waves will break on the surface, and k_L increases due to increased surface area, spray, and bubble entrainment (stripping). The value of k_L can be as high as 70 cm/hr in this range of wind speeds.

Liss and Slater (1974) suggest that a value for k_L of 20 cm/hr is applicable for gases with a molecular weight, MW, between 15 and 65, based on air/ocean transfer rates. For compounds with values outside this range, k_L can be corrected by using the equation:

$$k_L = 20\ [44/MW]^{-1/2} \quad \text{(cm/hr)} \tag{20}$$

However, this method is not well-established for high molecular weight compounds such as PCBs (Lyman et al., 1982). Schwarzenbach et al.(1979), suggest that mass transfer coefficients based on air/sea transfer rates may overestimate transfer in smaller bodies of water, such as lakes.

Liss and Slater (1974) have determined the ratio k_G/k_L to be approximately 96 for the air/sea interface. Mackay (1977) found this ratio ranged from 50 to 200 for other interfaces.

TABLE 2-1. EQUATIONS FOR CALCULATING k_L AND k_G

LIQUID PHASE QUIESCENT SURFACE:

1) Method of Springer et al. (1984):

a) For $0 < U_{10} < 3.25$ m/s and all F/d ratios

$$k_L = 2.78 \times 10^{-6} \left(\frac{D_w}{D_{ether}}\right)^{2/3} \tag{1}$$

b) For $U_{10} > 3.25$ m/s and $14 < F/d < 51.2$

$$k_L = [2.605 \times 10^{-9} (F/D) + 1.277 \times 10^{-7}]\, U_{10}^2 \left(\frac{D_w}{D_{ether}}\right)^{2/3} \tag{2}$$

c) For $U_{10} > 3.25$ m/s and $F/d > 51.2$

$$k_L = 2.611 \times 10^{-7}\, U_{10}^2 \left(\frac{D_w}{D_{ether}}\right)^{2/3} \tag{3}$$

where

k_L = liquid phase mass transfer coefficient (m/s)
U_{10} = windspeed at 10 m above the liquid surface (m/s)
D_w = diffusivity of the constituent in water (cm^2/s)
D_{ether} = diffusivity of ether in water (cm^2/s)
F = fetch, defined as linear distance across water body, in the direction of wind movement (m)
d = depth of the water body (m)

2) Method of Mackay and Yeun (1983):

a) For $U_{10} > 3.25$ and $F/d < 14$ and $U^* > 0.3$

$$k_L = 1.0 \times 10^{-6} + 34.1 \times 10^{-4}\, U^*\, Sc_L^{-0.5} \tag{4}$$

b) For $U_{10} > 3.25$ and $F/d < 14$ and $U^* < 0.3$

$$k_L = 1.0 \times 10^{-6} + 144 \times 10^{-4}\, U^{*2.2} Sc_L^{-0.5} \tag{5}$$

TABLE 2-1. EQUATIONS FOR CALCULATING k_L AND k_G (continued)

where

k_L = liquid phase mass transfer coefficient (m/s)
U^* = friction velocity (m/s) = $0.01\ U_{10}(6.1 + 0.63U_{10})^{0.5}$
Sc_L = Schmidt number on liquid side = $\frac{\mu_L}{\rho_L D_w}$
μ_L = viscosity of water (g/cm-s)
ρ_L = density of water (g/cm^3)
D_w = diffusivity of constituent in water (cm^2/s)

3) Method of Cohen et al. (1978):

a) For $V_{wind} < 3$ m/s

$$k_L \text{ approximately 2-3 cm/hr} \quad (6)$$

b) For 3 m/s $< V_{wind} <$ 10 m/s

$$k_L \text{ approximately 3-30 cm/hr} \quad (7)$$

c) For $V_{wind} > 3$ m/s

$$k_L \text{ approximately 30-70 cm/hr} \quad (8)$$

where

k_L = liquid phase mass transfer coefficient (cm/hr)

V_{wind} = velocity of wind (m/s)

4) Method of Liss and Slater (1974):

a) For gases with $15 < M < 65$

$$k_L = 20 \text{ cm/hr} \quad (9)$$

b) For gases with $M < 15$ or $M > 65$

$$k_L = 20\ (44/M)^{-1/2} \text{ cm/hr} \quad (10)$$

where

k_L = liquid phase mass transfer coefficient (cm/hr)

M = molecular weight (g/mol)

TABLE 2-1. EQUATIONS FOR CALCULATING k_L AND k_G (continued)

LIQUID PHASE TURBULENT SURFACE:

5) Method of Southworth (1979):
--Applicable to compounds with $10^{-5} < H < 10^{-3}$ atm-m^3/mol, and turbulent water bodies such as rivers.

a) $V_{wind} < 1.9$ m/s

$$k_L = 23.51 \left[\frac{V_{curr}^{0.969}}{Z^{0.673}}\right][32/M]^{1/2} \tag{11}$$

b) $1.9 < V_{wind} < 5.0$ m/s

$$k_L = 23.51\left[\frac{V_{curr}^{0.969}}{Z^{0.673}}\right][32/M]^{1/2}\ e^{0.526(V_{wind}-1.9)} \tag{12}$$

where

k_L = liquid phase mass transfer coefficient (cm/hr)
V_{wind} = velocity of wind (m/s)
V_{curr} = river flow velocity (m/s)
M = molecular weight (g/mol)
z = depth of river (m)

6) Method of Thibodeaux (1978):
--Applicable to turbulent surface impoundments, with aerators.

$$k_L = [8.22 \times 10^{-9}\ J\ (POWR)\ (1.024)^{T-20}\ O_t\ 10^6\ MW_L/Va_v\rho_L)]\ (D_w/D_{O_2,w})^{0.5} \tag{13}$$

where

k_L = liquid phase mass transfer coefficient (m/s)
J = oxygen transfer rating of surface aerator (lb O_2/h-hp)
POWR = total power to aerator (hp)
T = water temperature (^oC)
O_t = oxygen transfer correction factor
MW_L = molecular weight of liquid

TABLE 2-1. EQUATIONS FOR CALCULATING k_L AND k_G (continued)

V = volume affected by aeration (ft^3)
a_v = surface-to-volume ratio of surface impoundment (1/ft)
ρ_L = density of liquid (g/cm^3)
D_w = diffusivity of constituent in water (cm^2/s)
$D_{O_2,w}$ = diffusivity of oxygen in water (cm^2/s)

GAS PHASE

1) Method of Mackay and Matsugu (in U.S. EPA, 1987b):
--Applicable to quiescent water bodies.

$$k_G = 4.82 \times 10^{-3} \, U^{0.78} \, (Sc_G)^{-0.67} (d_e)^{-0.11} \quad (14)$$

where

k_G = gas phase mass transfer coefficient (m/s)
U = windspeed (m/s)
Sc_G = Schmidt number on gas side = $\dfrac{\mu_G}{\rho_G D_a}$
μ_G = viscosity of air (g/cm-s)
ρ_G = density of air (g/cm^3)
D_a = diffusivity of constituent in air (cm^2/s)
d_e = effective diameter of impoundment = $\left(\dfrac{4A}{\pi}\right)^{0.5}$ (m)
A = area of impoundment (m^2)

2) Method of Southworth et al. (1979):
--Applicable to compounds with $10^{-5} < H < 10^{-3}$ atm m^3/mol, and turbulent water bodies such as rivers.

$$k_G = 1137.5 \, (V_{wind} + V_{curr})[18/M]^{1/2} \quad (15)$$

where

k_G = gas phase mass transfer coefficient (cm/hr)
V_{wind} = velocity of wind (m/s)
V_{curr} = river flow velocity (m/s)
M = molecular weight (g/mol)

TABLE 2-1. EQUATIONS FOR CALCULATING k_L AND k_G (concluded)

3) Method of Reinhardt (1977):

--Applicable to turbulent surface impoundments, with aerators

$$k_G = 1.35 \times 10^{-7} R_e^{1.42} p^{0.4} Sc_G^{0.5} F_r^{-0.21} D_a MW_a/d \qquad (16)$$

where

k_G = gas phase mass transfer coefficient (m/s)

R_e = $d^2 w\rho a/\mu_a$ = Reynold's number

d = impeller diameter (cm)

w = rotational speed of impeller (rad/s)

ρ_a = density of air (g/cm^3)

μ_a = viscosity of air (g/cm s)

p = power number = $P_I \, g_c/(\rho_L d^{*5} w^3)$

P_I = power to impeller ($ft\text{-}lb_f/s$)

= 0.85 (POWR) (550 $ft\text{-}lb_f/s\text{-}hp$)/number of aerators, where 0.85 is the efficiency of the aerator motor

POWR = total power of the aerators (hp)

g_c = gravitational constant ($lb_m\text{-}ft/s^2/lb_f$)

ρ_L = density of liquid (lb/ft^3)

d^* = impeller diameter (ft)

Sc_G = Schmidt number on gas side = $\mu_a/\rho_a D_a$

F_r = Froude number = $d^* w^2/g_c$

D_a = diffusivity of constituent in air (cm^2/s)

MW_a = molecular weight of air

Thibodeaux (in Hwang, 1982) presents a method for estimating k_L for the case when the liquid is mechanically-aerated. Mass transfer generally increases significantly with aeration in comparison to transfer from a quiescent surface. Thibodeaux developed his model based on data from wastewater treatment basins from the pulp and paper industry. Thibodeaux's equations require two parameters which are not required under quiescent conditions; the oxygen transfer rating of the surface aerators and the total power to the aerators. The complete equations are presented in Table 2-1.

2.2.3.3.2 Gas-Phase Mass-Transfer Coefficients--Mackay and Matsugu (in Hwang, 1982) have developed a method for estimating the gas-phase mass-transfer coefficient based on experimentally determined volatilization rates for isopropyl benzene, gasoline, and water. In their equation, k_G is a function of the wind speed raised to a power of 0.78.

As discussed above, Southworth et al. (1979) developed a method for estimating k_G under turbulent conditions. The method is applicable only to compounds with a range of Henry's law coefficients between 10^{-5} and 10^{-3} atm-m^3/mol. The equations are presented in Table 2-1.

Reinhardt (1977) measured the gas-phase mass-transfer coefficient by absorbing ammonia into aqueous sulfuric acid. His equation can be used to estimate k_G for the turbulent portion of the liquid surface. The zones which are non-turbulent should be calculated using equations for quiescent conditions, as discussed above. Reinhardt's equation is applicable to flat-blade surface agitators, and requires several parameters related to the aerators, such as the power to the impeller, the impeller diameter and the power number. The equation is presented in Table 2-1.

Other methods for determining k_G and k_L are presented in Breton et al. (1984). For the sake of brevity, they are not included in this report.

2.2.3.4 Relation of Mass Transfer to Diffusion--

In general, the overall mass transfer coefficients for many volatile solutes have been shown to be proportional to one another (Tsivoglou et al., 1965, 1968; Matter-Mullër et al., 1980, 1981; Smith et al., 1980). Because oxygen is volatile under most conditions, and because a large volume of data exists on oxygen transfer rates, oxygen is typically used as the reference compound (Roberts et al., 1984). The relationship between the liquid-phase mass transfer coefficients can be expressed as:

$$(K_L a)_i = \psi_i \, (K_L a)_{O_2} \qquad (21)$$

where

$(K_L a)_i$ = overall transfer rate constant of component i (1/sec)

ψ_i = transfer rate proportionality constant (1/sec)

$(K_L a)_{O_2}$ = overall mass transfer rate of oxygen in the liquid phase (1/sec)

This equation appears to be valid for a wide range of volatile solutes (Roberts and Dandliker, 1983; Roberts, 1984). The proportionality constant, ψ_i, is approximately constant, independent of temperature or turbulence. It can be measured directly or estimated from its relationship to the liquid-phase mass transfer coefficients or the liquid-phase diffusivity ratio:

$$\psi_i = \frac{k_{L,i}}{k_{L,O_2}} = \left(\frac{Di}{D_{O_2}}\right)^n \tag{22}$$

where

k_{L,O_2} = liquid-phase mass transfer ratio for oxygen (cm/s)

$k_{L,i}$ = liquid-phase mass transfer ratio for component i (cm/s)

D_i = diffusivity of compound i in water (cm^2/s)

D_{O_2} = diffusivity of oxygen in water (cm^2/s)

n = exponent

Although the value of n may vary from 0.5 to 1 by the penetration theory, reported measured values range from 0.61 to 0.66 (Roberts and Dandlicker, 1983; Smith et al., 1980). Furthermore, Equation 22 can be used to estimate the mass transfer coefficient for a given compound, i, from a reference compound, j, if the diffusivities are known. For highly volatile compounds, the gas-phase resistance is negligible, and the overall mass transfer rate can be expressed:

$$K_La = k_La \tag{23}$$

Under these circumstances, the liquid-phase diffusivity coefficient can be estimated by the equation:

$$k_La_i = \psi_i \; K_La_{O_2} \tag{24}$$

A method for estimating $K_La_{O_2}$ is presented in Barton (1984). In this derivation, n is assumed to be 0.6, and the basin is mechanically-aerated. The equation is:

$$K_La_{O_2} = \frac{454 \; N_o \; HP \; \alpha \; \theta^{(T-20)}}{C_s^* \; V} \tag{25}$$

where

N_o = standard oxygen transfer rate (lbs O_2/ HP-hr)

HP = total aeration horsepower (HP)

α, θ =dissolved oxygen correction factors (dimensionless)

C_s^* = saturation concentration at 20° (mg/l)

V = basin volume (10^6 liters)

D_i can be estimated by the methods discussed in Section 2.2.3.5, below. Values for the diffusivity of oxygen, D_{O_2}, are widely available.

2.2.3.5 Diffusion Coefficients--

Several methods have been developed for estimating diffusion coefficients in air and water.

2.2.3.5.1 Diffusivity in Gas--The kinetic theory of gases provides the foundation for the development of a widely-used (Roberts et al., 1984) expression for the diffusion coefficient in air (Chapman and Enskog, in Reid et al., 1977):

$$\wp_{BA} = 1.858 \times 10^{-3} \frac{T^{1.5}\sqrt{M_r}}{P\sigma_{AB}{}^2\ \omega} \qquad (26)$$

where

$\wp_{BA}$ = gas diffusion coefficient in air (cm^2/s)

T = temperature (K)

$M_r = \dfrac{(M_A + M_B)}{M_A\ M_B}$

M_A = molecular weight of air (g/mol)

M_B = molecular weight of compound B (g/mol)

P = pressure (atm)

σ_{AB} = characteristic length

ω = collision integral

Methods for estimating the air diffusion coefficient are based on this equation. There are numerous formulas for estimating $\wp_{BA}$, nine of which are presented in Lyman et al. (1982). Lyman et al. (1982) recommends two of these methods based on their relative ease of use, availability of input data, and accuracy of results. The first is the method of Fuller, Schettler and Giddings (1966), which can be used for non-polar gases at low to moderate temperatures, and aliphatics and aromatics. It should not be used with polar acids and glycols. The second equation, proposed by Wilke and Lee (1955), is very similar to Equation 22, and can be used for a wider range of compounds than the method proposed by Fuller, Schettler and Giddings. Wilke and Lee's method is much more accurate for nitriles, aromatic esters and glycols, and can be used over a larger temperature range (Lyman et al., 1982). Both methods are presented in Table 2-2. A less complex method by Spivey et al. (1984) for estimating the air diffusion coefficient is presented in U.S. EPA (1987b). Because it is applicable only at a temperature of 300 ^{o}K, it is not presented here.

2.2.3.5.2 Diffusivity in Water--The Stokes-Einstein equation, which was derived for large, spherical molecules diffusing in a continuous solution, is the theoretical basis for estimation methods for liquid diffusion coefficients. This equation is:

$$\mathcal{D}_{AB} = \frac{RT}{6\eta_w \, r_B} \qquad (27)$$

where

$\mathcal{D}_{AB}$ = diffusion coefficient of compound B in compound A (cm^2/s)

η_w = viscosity of water (cp)

r_B = radius of molecule B (cm)

T = temperature (K)

R = universal gas constant ($atm\text{-}m^3/mol\text{-}K$)

Experimental results have deviated from this equation due primarily to the variations in the molecular size and shape of the compounds. It has been suggested that $\mathcal{D}_{AB}$ is actually a function of η_w raised to a power between -0.45 and -0.66 (Reid et al., 1977; Lyman et al., 1982). However, the equations used for estimation of diffusion coefficients generally assume that $\mathcal{D}_{AB}$ is a function of the size of the compound, viscosity of the solution and the temperature. While information on the dependence of the apparent diffusion coefficient, D_{AB}, on temperature over a wide range of temperatures is not conclusive, a linear dependence is a reasonable assumption over the temperature range normally found in the environment (Lyman et al., 1982).

Several methods have been proposed for estimating diffusivity in water, and the equations for six of these methods are presented Lyman et al. (1982). All of the methods assume that the solution is dilute (i.e., the concentration of the solute is less than 0.05 molar). The diffusion coefficient is dependent on concentration, but this effect can usually be neglected in dilute solutions. However, experimental data should be checked to see if D_{AB} or k_L (related to D_{AB} by $k_L = D_{AB}/\delta$) vary with concentration (Roberts et al., 1984).

The Stokes-Einstein equation was modified by Wilke and Chang (1955), who developed a formula, fitted to experimental data, for estimating the liquid diffusion coefficient. Their method requires a solution association constant, ϕ, and the molar volume of compound B, V_B, in addition to the parameters specified in the Stokes-Einstein equation. Hayduk and Laudie (1974), suggest

TABLE 2-2. METHODS FOR ESTIMATING DIFFUSIVITY IN WATER AND GAS

DIFFUSIVITY IN GAS:

1) Method of Fuller, Schettler and Giddings (1966):
--See text for applicability.

Basic equation:

$$\mathcal{D}_{BA} = \frac{10^{-3}T^{1.75}\sqrt{M_r}}{P(V_A^{1/3} + V_B^{1/3})^2} \tag{1}$$

where

$\mathcal{D}_{BA}$ = gas diffusion coefficient in air (cm^2/s)
T = temperature (K)
$M_r = \frac{(M_A + M_B)}{M_A M_B}$
M_A = molecular weight of air (g/mol)
M_B = molecular weight of compound B (g/mol)
P = pressure (atm)
V_A = diffusion volume of air (cm^3/s)
V_B = diffusion volume of compound B (cm^3/s)

The molal volume of air, V_A, is 20.1 cm^3/mol (Jarvis and Lugg, 1968). V_B can be computed by a method presented in Reid et al., (1977). In this method, the LaBas molar volume, V_B', is calculated by summing incremental values for all atoms present in the compound. These incremental values are given for common elements such as oxygen, hydrogen and carbon. However, the LaBas molar volume of some compounds may not be estimatable, since atoms in their composition may not be included in the tables. The diffusion volume is approximated as 85-90% of the LaBas molar volume, $V_B = (0.85\text{-}0.90)V_B'$.

2) Method of Wilke and Lee (1955):
--See text for applicability.

Basic equation:

$$\mathcal{D}_{BA} = \frac{B'T^{1.5}\sqrt{M_r}}{P\sigma_{AB}^2\ \Omega} \tag{2}$$

TABLE 2-2. METHODS FOR ESTIMATING DIFFUSIVITY IN WATER AND GAS (concluded)

where

$$B' = 0.00217 - 0.00050 \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2}$$

σ_{AB} = characteristic length

Ω = collision integral

and the other parameters are defined as in equation 1.

σ_{AB} and Ω can be calculated by a method presented in Lyman et al. (1982) and in Wilke and Lee (1955). The calculation of these parameters requires values from several tables included in Wilke and Lee (1955), as well as knowledge of the molecular weight, boiling point, and molal volume of compound B.

DIFFUSIVITY IN WATER:

3) Method of Hayduk and Laudie (1974):
--See text for applicability.

Basic equation:

$$\wp_{BW} = \frac{13.26 \times 10^{-5}}{(\eta_w)^{1.14} (V_B')^{0.589}} \qquad (3)$$

where

$\wp_{BW}$ = diffusion coefficient of compound B in water (cm^2/s)
η_w = viscosity of water at temperature of system (cp)
V_B' = LaBas molal volume (cm^3/s)

The LaBas molal volume can be calculated by a method presented in Reid et al. (1977) as discussed above.

that the value of ϕ in the Wilke and Chang method is too high. They were able to reduce the average absolute error 3% from the Wilke-Chang estimates by decreasing the value of ϕ. The Hayduk and Laudie method produces the smallest absolute error of any of the methods presented in Lyman et al. (1982). It contains a manageable number of parameters, and is the method recommended by the authors. Therefore, the equation for the Hayduk method is presented in Table 2-2. There are many other methods for estimating the diffusion coefficient, some of which are less complicated. A simpler method by Spivey et al. (1984) is discussed briefly in U.S. EPA, 1987b. The method assumes a temperature of 300 ^{o}K and thus, is of limited applicability.

2.2.4 Importance of Volatilization from Water as a Pathway for Removal of Contaminants from Sites

Volatilization from water is considered an important pathway for removal of volatile organics from several types of biological treatment facilities (U.S. EPA,1987b). It is a potentially significant pathway in surface impoundments, as well as in aerated and non-aerated treatment plants. The extent to which a volatile organic will volatilize is dependent on a wide variety of factors, including the nature of the contaminant, the type of treatment process involved, the degree of aeration in the treatment process, and the amount of biodegradation or other processes occurring. Models have been created to allow for estimation of volatilization rates under different conditions. The models will be discussed in the following chapters.

2.2.5 Stripping Process

Stripping is an active volatilization process. It is distinguished from passive volatilization by being an energy-intensive process. Stripping is the transfer of dissolved compounds to the gas phase at dispersed interfaces such as the surface of water droplets or air bubbles. These droplets or air bubbles could be generated by surface or subsurface aeration, or turbulence in a water body.

Stripping may occur naturally, or it may be induced by mechanical aeration. The stripping process is commonly used to remove ammonia, hydrogen sulfide, sulfur dioxide and phenol from water supplies, and is also used to clean waters contaminated by leakage from chemical storage facilities and landfills (Tchobanoglous and Schroeder, 1985). Of course, removal of contaminants from water by this process causes the transfer of these contaminants into the atmosphere.

2.2.6 Factors Affecting Stripping Rates

The rates of stripping from water are a function of similar properties and conditions as those which affect the rates of the related process of passive volatilization. Rates can be estimated based on measurable properties of the contaminant, such as its aqueous solubility, vapor pressure, Henry's law coefficient, and diffusion coefficient, the characteristics of the water body, the presence of other compounds, as well as the conditions in the atmosphere above the water body. The theories of mass transfer across the liquid/air interface are applicable to the stripping process.

The rate of change of concentration of a compound in a completely-mixed tank due to stripping, can be written (Barton, 1984):

$$\frac{dC_{Li}}{dt} = K_L^s a(C_{Li}^* - C_{Li}) \tag{28}$$

where

C_{Li} = effluent concentration of compound i (mg/m^3)

$K_L^s a$ = overall mass transfer coefficient from the liquid phase (1/hr)

C_{Li}^* = liquid phase concentration of compound i in equilibrium with the gas phase (mg/m^3)

Applying the equations developed in Section 2.2.2.1 for the two-film theory, the overall mass transfer coefficient is related to the liquid and gas phase mass transfer coefficient by:

$$\frac{1}{K_L^s a} = \frac{1}{k_L^s a} + \frac{1}{H_c k_G^s a} \tag{29}$$

Equations for estimating mass transfer coefficients for the stripping process are similar to those discussed above for passive volatilization. The specific surface area, a, for stripping processes is calculated as the total air bubble surface area divided by the reactor liquid volume (Lee and Stensel, 1986). When the resistance in the gas phase is negligible, the liquid-phase transfer coefficient, $k_L^s a$, can be estimated from Equation 21:

$$k_L^s a_i = \psi_i \; K_L a_{O_2} \tag{30}$$

where ψ_i and $K_L a_{O_2}$ can be estimated as discussed in Section 2.2.3.5.

An alternative method for determining the stripping rate constant is presented in Troung and Blackburn (1984) and is discussed in Section 4.1.3.1.

Stripping rates can be estimated for both surface and subsurface aeration. In surface aeration, the transfer occurs directly to the atmosphere from spray droplets. A common assumption is that the concentration of the compound in the atmosphere above the basin is negligible. Thus, C_{Li}^* in Equation 28 is zero. This is generally considered a good assumption (Roberts et al., 1984), which simplifies the equation to:

$$\frac{dC_{Li}}{dt} = - K_L^s a(C_{Li}) \tag{31}$$

In subsurface aeration, the transfer of the compound occurs from the liquid into the rising bubble, which complicates the mass transfer equations. The saturation of the air within the bubble must be considered since partial saturation should occur for volatile compounds (Barton, 1984). A method for determining the fractional saturation of the air bubble is presented in Munz and Roberts (1982).

2.2.7 Importance of Stripping as a Pathway for Removal of Contaminants from Sites

Stripping may be a significant pathway for removal of volatile organics from biological treatment facilities when there is turbulence at the air/water interface, or the system is aerated by surface or subsurface methods. It is a potentially significant pathway in surface impoundments, as well as in aerated treatment plants. The extent to which stripping processes will be a pathway for removal of a contaminant from a site is dependent on the nature of the contaminant, the type of treatment process involved, the type and degree of aeration in the treatment process, and the amount of passive volatilization, biodegradation or other processes occurring.

2.3 VOLATILIZATION AT A SOIL-WATER INTERFACE

2.3.1 Volatilization Process

Volatilization from soil is conceptually more complex than volatilization from water, since a contaminant in soil may be partitioned between the soil water, soil air, and soil matrix itself (Lyman et al., 1982). Volatilization is one of several transport processes which occur between these compartments, as the contaminant might transfer from a sorbed state in the soil, into solution in the soil water, into the vapor phase in the soil air, and then into the atmosphere. The concentration of the chemical in the soil air in equilibrium with the soil water can be determined by Henry's law. The mass transport of the contaminant from the soil water to the soil air can be estimated by methods for determining rates of volatilization from the air/water interface (Section 2.2). However, when there is little evaporation occurring in the soil, the transport of the chemical through the soil is primarily by diffusion processes, which are discussed below.

2.3.2 Factors Affecting Volatilization from Soil

The volatilization rate from soil is a function of the concentration and properties of the contaminant, and can be estimated using the contaminant's vapor pressure and solubility. The rate also depends on the conditions present in the soil, including temperature, porosity, moisture content, clay and organic content, and on the properties of the air in the region near the soil, such as the temperature, relative humidity and flow of air over the surface. Some of the most important factors influencing the volatilization rate are discussed below, but there are numerous other effects which influence the rate. Some of these are easily quantified, and others are more difficult to determine.

The vapor density, the concentration of the compound in the soil air, directly determines the volatilization rate (Lyman et al., 1982). The vapor density generally increases with increasing concentration of the compound at the evaporating surface of the soil (Spencer et al., 1973), with increasing water content in the soil and increasing temperature (Guenzi and Beard, 1974). The vapor density typically decreases when the organic content of the soil is increased (Spencer, 1970).

The process of adsorption, discussed in Section 2.4, influences the volatilization rate by affecting the vapor density (Spencer and Cliath, 1975). Increased sorption reduces the amount of contaminant in the soil water, thereby decreasing the amount available for volatilization. The concentration of the chemical in the soil water controls the vapor density, which is directly related to the rate of volatilization.

Another process which can be important in determining the rate of volatilization from soil is the wick effect. This refers to the transport of a chemical from the solid matrix to the soil surface by capillary action. Water is lost at the surface by evaporation, and more water moves up to replenish the lost water. If the chemical is relatively less volatile than water, this process can cause an increase in concentration of the chemical near the soil surface, which is likely to increase the rate of volatilization of the chemical. This process is discussed in detail by Hartley (1969).

2.3.3 Estimating Parameters Used in Soil Volatilization Models

2.3.3.1 Diffusion Coefficients--

Diffusion through the soil water, or soil matrix is a much slower process than gaseous diffusion (Hamaker,1972). Typically, the vapor phase diffusion coefficient is on the order of 10^4 greater than the coefficient for the liquid phase (Lyman et al., 1982). Diffusion coefficients may be estimated by the methods discussed in Section 2.2.3.4. An alternative method, which includes the soil porosity in the calculations is presented by Farmer et al. (1980). The apparent vapor-phase diffusion coefficient is given by:

$$D'_v = D_v \, (s^{10/3}/s_t^{\,2}) \qquad (32)$$

where

D'_v = apparent vapor-phase diffusion coefficient (cm^2/s)

D_v = vapor-phase diffusion coefficient in air (cm^2/s)

s = air-filled porosity

s_t = total porosity (air + water)

For dry soil, when $s = s_t$, the equation reduces to:

$$D'_v = D_v \, (s_t^{\,1.33}) \qquad (33)$$

Hamaker (1972) presents a method by which vapor phase diffusion coefficients at different temperatures and pressures can be related:

$$D_1/D_2 = P_2/P_1 \, (T_1/T_2)^m \qquad (34)$$

where

D_1 = diffusion coefficient for compound at P_1, T_1 (cm^2/s)

D_2 = diffusion coefficient for compound at P_2, T_2 (cm^2/s)

$P_{1,2}$ = ambient total pressure (atm)

$T_{1,2}$ = temperature (K)

The exponent, m, is theoretically 1.5 and is measured experimentally as 1.75 to 2.0 (Lyman et al., 1982).

Vapor-phase diffusion coefficients can also be related by their molecular weights, M, (Lyman et al., 1982):

$$D_1/D_2 = \sqrt{M_2/M_1} \tag{35}$$

2.3.4 Importance of Volatilization from Soil as a Pathway for Removal of Contaminants from Sites

Volatilization from soil is potentially a significant pathway for removal of volatile organics from biological treatment processes involving soil, such as landfarming facilities (U.S. EPA, 1987b). There are numerous factors which can affect the importance of volatilization from soil as a pathway, including the type of site and the procedures for handling the waste at the site. For example, volatilization rates will differ for chemicals applied directly to the soil surface as compared to chemicals which are incorporated into the soil matrix, by some process such as tilling. Different models for estimation of air emissions have been developed for these different conditions and are discussed in the following chapters.

2.4 ADSORPTION

2.4.1 Adsorption Processes

Adsorption occurs when a chemical in the solution phase becomes attached to the solid phase. Sorption may be the result of chemical adsorption, physical adsorption (van der Waals forces) or hydrogen bonding (Guenzi and Beard, 1974). When adsorption is a significant pathway for the removal of a contaminant, there is a higher concentration of the contaminant at the soil surface than is present in the bulk aqueous solution.

The process of adsorption can remove a chemical from the solution, in a temporary or a permanent sense (Mackay, 1977). A contaminant may become adsorbed to a solid surface, remain in a sorbed state for a period of time, and then desorb and reenter the solution. This equilibrium adsorption-desorption process is governed by two rates: the rate of adsorption is the rate at which molecules of a chemical transfer from the liquid to the solid phase; the desorption rate is the rate at which chemicals transfer from their sorbed state in the solid phase, back to the liquid. The rate of adsorption increases as the concentration of the dissolved chemical in the solution increases, whereas the desorption rate increases when the concentration of the dissolved species drops. The system is in equilibrium when the rates of adsorption and desorption are equal.

The adsorption process affects the rates of removal of contaminants from a site by other pathways. Adsorption is directly related to the process of volatilization, since sorption reduces the amount of a chemical available for volatilization. Biodegradation processes may be affected by adsorption. For example, some chemicals may be trapped between clay particles in pores which are too small for microorganisms to penetrate (Alexander, 1973), or adsorption of the organic chemicals onto suspended solids and biological matter may significantly reduce the amount of substrate available for biodegradation (Swisher, 1970). The effect of adsorption on hydrolysis and photochemical decomposition is not precisely known, other than that it removes a fraction of the chemical which might otherwise be affected by these processes.

2.4.2 Adsorption Isotherm Models

Adsorption equilibrium relationships, commonly called isotherms, relate the concentration of the chemical in the liquid and solid phases. Isotherms are generally measured experimentally; a known concentration of the adsorbent (solid) is allowed to equilibrate with the chemical of interest in solution, and the concentrations are measured. This data can then be fitted to one of the isotherm models, which describes these relationships at a given temperature. The three most common models are the linear, Freundlich, and Langmuir models (Freeman, 1989).

The linear model is most often used, since the assumption of a linear isotherm simplifies the description of adsorption, and generally does not produce significant errors in determining the partitioning of the compound in the environment (Rao et al., 1982). However, a linear isotherm model should not be used for extrapolation of estimated "linear" sorptive behavior significantly beyond the compound's observed fugacity range or when the strongly-sorbed compound is bound by highly site-specific mechanisms (Karickhoff, 1984). In these cases, the use of a nonlinear isotherm model should be considered.

2.4.2.1 Linear Adsorption Isotherm--

The linear adsorption isotherm can be written:

$$\frac{X}{M} = K_d C \qquad (36)$$

where

X = mass of chemical adsorbed (μg)

M = mass of adsorbent (g)

K_d = linear adsorption coefficient ((μg/g)/(μg/ml))

C = concentration of chemical in solution at equilibrium (μg/ml)

2.4.2.2 Freundlich Adsorption Isotherm--

The Freundlich adsorption isotherm equation is similar to the linear isotherm equation except that adsorption is a function of C raised to a power of 1/n, where n is a dimensionless empirical constant. The linear model can be viewed as a specific case of the Freundlich isotherm when n=1.0, and the adsorption is therefore linearly dependent on C. The Freundlich equation can be written as follows:

$$\frac{X}{M} = K_f \, C^{1/n} \tag{37}$$

where

K_f = Freundlich adsorption coefficient ((μg/g)/(μg/ml) when n = 1)

Values for 1/n generally range from 0.7 to 1.1 although Hamker and Thompson (1972) report values as low as 0.3 and as high as 1.7. When values are not available, a value of 1.0 is typically assumed, since no methods are available to estimate 1/n (Lyman et al., 1982). Some authors use a single parameter, n, in place of 1/n. Care should be taken that the value of n is consistent with the form of the equation used.

2.4.2.3 Langmuir Adsorption Isotherm--

The Langmuir isotherm model was developed for single-layer adsorption and is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface (Calabrese and Kostecki, 1988). It can be derived from kinetic rate theory applied to rates of adsorption and desorption. The equations can be written as follows (U.S. EPA, 1987b):

$$\text{Rate of adsorption} = K_1 \, C \, (1-f) \tag{38}$$

where

K_1 = rate constant for adsorption (g/s)

f = fraction of adsorption sites occupied (dimensionless)

and

$$\text{Rate of desorption} = K_2 \, f \tag{39}$$

where

K_2 - rate constant for desorption (g/s)

At equilibrium, these two rates are equal. Rearranging the equations:

$$f = \frac{K_1 C}{K_1 C + K_2} \tag{40}$$

2.4.3 Factors Affecting Adsorption

The extent to which a chemical partitions itself between the liquid and solid phases is dependent on several factors. Adsorption rates are influenced by several inherent properties of the compound and soil matrix. The chemical structure and configuration, charge, molecular size, polarity, acidity or basicity of the molecule can all affect the nature of the adsorption (Helling and Dragun, 1981). Several properties can be measured to estimate these intrinsic chemical properties, such as the water solubility or octanol/water partition coefficient.

In general, the tendency of a chemical to be adsorbed can be related to a parameter, K_{oc}, which is relatively independent of the properties and characteristics of the soil or sediment. The equation for K_{oc} is described in Lyman et al. (1982):

$$K_{oc} = \frac{\mu\text{g of chemical adsorbed/ g organic carbon in soil or sediment}}{\mu\text{g/ml of the chemical in the solution}} \tag{41}$$

Numerous studies of the factors influencing K_d and K_{oc} are available, including Adams (1972), Hamaker and Thompson (1972), Freed and Haque (1973), Huang (1974), Karickhoff et al. (1979), and Rao and Davidson (1980). The organic carbon content usually provides the most significant correlation with the adsorption coefficient. In general, K_{oc} is relatively independent of other soil characteristics such as the clay content, surface area, cation exchange capacity, and pH. However, under certain conditions, adsorption can occur even when soils or sediments contain no organic carbon. In these cases, K_{oc} values should probably not be used to estimate the adsorption coefficient, K_d. Unfortunately, no methods are currently available for estimation of adsorption coefficients under these conditions (Lyman et al., 1982).

Coefficients of adsorption are also functions of the environmental conditions in the soil or sediments. Adsorption coefficients typically decrease with increasing dissolved organic matter, which may be due to increased competition for the adsorption sites (Wershaw et al., 1969; Poirrier et al., 1972; Hassett and Anderson, 1978), with increasing temperature (Bailey and White, 1964), and with increasing salinity (Hamaker and Thompson, 1972). Changes in pH will only affect chemicals which are easily ionized; other contaminants will be unaffected (Ahlrichs, 1972; Hamaker and Thompson, 1972; Poinke and Chesters, 1973). Weak acids and bases are the most sensitive to pH changes normally encountered in soils and surface waters (Lyman et al., 1982). The nature of the soil or sediment can affect the adsorption process; fine silt and clay particles have a much greater tendency to sorb chemicals than do other particles.

2.4.4 Estimation of Parameters Used in Adsorption Equations

2.4.4.1 The Adsorption Coefficient Based on Organic Carbon Content--

K_{oc} can be determined from adsorption-isotherm experiments where the data is fitted to the linear isotherm equation to obtain a value for K_d. K_{oc} is usually not calculated using Freundlich constants due to the uncertainty associated with the value of n. Therefore, a linear isotherm is assumed, and the equation for K_{oc} can be written:

$$K_{oc} = \frac{K_d}{\%oc} \times 100 \qquad (42)$$

where

K_d = linear adsorption coefficient ((µg/g)/(µg/ml))

K_{oc} = adsorption coefficient based on organic carbon content ((µg/g)/(µg/ml))

%oc = the percentage organic carbon contained in the soil or sediment

There are many published values for K_{oc}, primarily for pesticides and, to a lesser degree, aromatic and polycyclic aromatic compounds. Lyman et al. (1982) list ten different references which are recommended. However, if measured values of K_{oc} are not available, this parameter can be estimated by one of the numerous methods presented in Lyman et al. (1982). All of these methods involve empirical relationships between K_{oc} and some other property of the chemical such as the water solubility, S, the octanol-water partition coefficient, K_{ow}, or the bioconcentration factor for aquatic life, BCF. Lyman et al. (1982) tabulate 12 regression equations obtained from data sets of different classes of chemicals, and present guidelines for selecting an accurate and applicable equation for a particular chemical.

2.4.4.2 K_d and X/m--

If a value of K_{oc} has been determined by one of the methods presented above, K_d can be calculated easily by rearranging Equation 42:

$$K_d = \frac{K_{oc}}{100} \times (\%oc) \qquad (43)$$

The amount of chemical adsorbed, X, can be calculated from Equation 36 if the concentration of the chemical in solution is known, and equilibrium is assumed.

Extrapolation of laboratory-derived equations for soil-chemical interactions to the field should be done with care. Models which predict soil adsorption coefficients may differ from observed values by an order of magnitude (Dragun and Helling, 1981). The methods of estimating K_{oc}, K_d and X/m presented above assume a linear isotherm and reversible adsorption, which may not be entirely accurate. Lyman et al. (1982) present a table of the errors to be expected from the use of a linear isotherm. A discussion of the possible error involved in the assumption of reversible adsorption is found in Rao and Davidson (1980).

2.4.5 Importance of Adsorption as a Pathway for Removal of Contaminants from Sites

Adsorption is considered a pathway for removal of contaminants in both aerated and non-aerated wastewater treatment plants, although for volatile and semi-volatile compounds, it is of secondary importance compared to the processes of volatilization and biodegradation. Adsorption is particularly significant when large loadings of suspended solids and oils occur. Adsorption also occurs at land treatment facilities, although it is not considered a major pathway for organics removal. It is considered of negligible importance as a pathway for surface impoundments and landfills (U.S. EPA, 1987b).

2.5 MIGRATION

2.5.1 Migration Processes

2.5.1.1 Leaching, Percolation and Capillary Flow--

Contaminants in land treatment facilities may be leached by percolating water derived from precipitation. The liquid derived from this process is known as leachate, and it may be rich in inorganic and organic contaminants. This leachate generally migrates downward and outward from the site (Freeze and Cherry, 1979), and thus, could potentially threaten groundwater resources. In contrast, capillary flow transports the chemicals through the unsaturated zone toward the surface (U.S. EPA,1987b). The rates of these opposing processes will determine the rate and direction of transport of the chemical.

2.5.2 Factors Affecting Migration

Migration of contaminants in saturated and unsaturated soil depends upon the properties of the soil, such as its adsorptive properties, the nature of the contaminant and the rate at which chemicals and fluids move through the soil. The leachability of a chemical is a function of the soil texture, cation exchange capacity, organic content, amount and intensity of precipitation, and the properties of the chemical itself (Hornick, 1982). Some chemicals are easily transported by the downward-moving fluids, and others will remain in place.

2.5.3 Importance of Migration as a Pathway for Removal of Contaminants from Sites

Migration should be considered a potentially significant pathway for removal of contaminants from in-situ hazardous waste treatment processes. Migration of chemicals from a site has caused numerous groundwater contamination problems in the United States and other countries. Several methods are available for containment and treatment of the contaminated groundwater, which can reduce the migration of the chemical from the site.

If in-situ bioreclamation processes are excluded, migration is considered to be a negligible pathway for removal of contaminants from properly sited, operated and maintained hazardous waste treatment and disposal facilities (EPA, 1987). However, many older sites are poorly situated or operated, and even the new sites are fallible. Under ideal conditions, contamination of groundwater by migration of contaminants from a TSDF can be avoided. However, it is not always economically and politically feasible to situate a land treatment facility in an area which has ideal hydrogeological characteristics to prevent migration.

2.6 RUNOFF

2.6.1 Runoff Processes

During a rainfall event, water initially begins to saturate and infiltrate the upper layers of the soil. However, if the rainfall is of significant intensity and duration, water will begin to pool on the surface, and then run off the surface of the soil in small channels. Contaminants removed from the site may either be dissolved in the runoff water, or transported on soil particles which are also removed by the process of erosion. This transport of contaminants away from the site can potentially threaten water supplies.

2.6.2 Factors Affecting Runoff

The rate of removal of a contaminant from a site by runoff depends on the characteristics of the soil and the contaminant, as well as on the intensity and duration of the precipitation, and on the nature of the drainage basin. Many factors affect the process of saturation and infiltration of soils, such as the soil porosity, organic content, and the initial moisture content in the soil. The evapotranspiration rate will also significantly affect these processes. The characteristics of the drainage basin are important, including its size, shape, topography and land use (U.S. EPA, 1987b). The properties of the chemical will also determine its fate such as its size, water solubility, and tendency to sorb onto solid particles.

2.6.3 Importance of Runoff as a Pathway for Removal of Contaminants from Sites

Runoff should be considered, along with migration, as a potentially significant pathway for removal of contaminants from in situ bioremediation facilities. Contaminants near the surface may be transported off-site by this process, which can lead to contaminated surface water and, if it reenters the subsurface, groundwater supplies.

Runoff is considered a negligible pathway for removal of contaminants from a properly sited, operated and maintained hazardous waste treatment or disposal facility (U.S. EPA, 1987b).

2.7 BIOLOGICAL DECOMPOSITION

2.7.1 Biodegradation Processes

Biodegradation is an important process for the breakdown of organic compounds in aqueous systems and soils. The study of the rates of biodegradation of organic compounds is still in its infancy; most of the research is descriptive, focusing on identification of the organisms responsible for biodegradation, the metabolic products and classification of metabolic pathways. The process of biodegradation is complex, and the variables which control the rates are not well understood. Quantitative data are scarce and not easily accessible (Lyman et al., 1982).

Although higher-order plants and animals can metabolize some compounds, microorganisms are the most significant group involved in biodegradation processes. They often break down chemicals into simpler forms, which can then be metabolized by higher organisms (Dagley et al., 1972; Turner et al., 1984). Microorganisms which are predominately responsible for biodegradation are heterotrophic bacteria, some autotropic bacteria, fungi, and certain protozoa (Alexander, 1971). Under different environmental conditions, different microorganisms will dominate the degradation of organics. For example, bacterial microorganisms alone can account for up to 65% of the total metabolism in a soil community which is alkaline to slightly acidic (Howard et al., 1975), but are relatively inactive in acid soils. However, fungi thrive in acidic soils, and would dominate the metabolism of organic chemicals under these circumstances (Stotzky, 1974).

In the treatment of organic wastes, two biodegradation processes are commonly used: aerobic mineralization and anaerobic digestion. The first process is the breakdown of organic material into inorganic substances. Anaerobic digestion is the process of fermentation to methane and CO_2. Activated-sludge and trickling-filter treatment are two processes, which are usually aerobic (Lyman et al., 1982). They are discussed in detail in the following chapters. Anaerobic digestion is typically used for sludge stabilization (Reed, 1975).

2.7.2 Factors Affecting Biological Decomposition

The factors which influence the rate of biodegradation can be classified into two categories: 1) those that determine the availability and concentration of the organic material to be degraded and that affect the size and activity of the microbial population, and 2) those that directly control the reaction rate itself (Lyman et al., 1982).

The biodegradability of a compound can be related, in part, to its molecular characteristics. In general, water-soluble compounds are biodegraded more quickly than water-insoluble compounds although the explanation of this effect is not clear (Alexander, 1965; 1973). Several methods of estimating the biodegradability of a compound have been related to the BOD (biochemical oxygen demand) and the COD (chemical oxygen demand). Lyman et al. (1982) classify several categories of biodegradability based on the ratio of BOD/COD. Pitter (1976) presents results from a test which was developed to correlate COD decrease with biodegradability of organic compounds. Several authors have observed a correlation between rates of hydrolysis and biodegradability for a limited number of chemicals (Baughman et al., 1980; Wolfe, 1980; Tabak et al., 1964)

The nature and distribution of the microorganisms involved also affect the rate of biodegradation. Different microorganisms metabolize the same substrate at different rates. The concentration of microorganisms has a significant affect on the rate over the short term. Over longer periods of time, the concentration is not as significant in determining rates, since there are typically rapid increases in species capable of metabolizing the compound (Lyman et al., 1982).

The process of biodegradation is complex and the variables which affect the rates of biodegradation may affect different species in different ways. For example, the concentration of substrate available is thought to directly affect biodegradation rates. If the substrate concentration is too low, biological decomposition may be limited. However, if it is too high, the concentration may be toxic, or inhibit metabolism (Domsch, 1970; Parr, 1974; Anderson, 1978). The range of concentrations which will allow significant biodegradation varies depending on the chemical to be degraded, and on the species of microorganisms present (Lyman et al., 1982). This dependency on the chemical and species increase the uncertainty involved in extrapolating data based on one set of conditions to a different set of conditions.

Environmental conditions also greatly affect microbial activity. Temperature is typically a primary factor in controlling reactions. All species have a specific range of temperatures within which microbial growth can occur. Rates of biological reactions generally increase with increasing temperature within this range (Lyman et al., 1982). The acidity or basicity of the soil can also influence the growth of microorganisms. Most microorganisms require a certain level of moisture in the soil, although some species can tolerate the drying of the soil for periods of time. The amount of oxygen available determines whether conditions will be aerobic or anaerobic. Severe reductions in oxygen in an aerobic environment will retard growth (Larson, 1980). However, under anaerobic conditions, the presence of even small amounts of oxygen will limit microbial growth (Brook, 1970).

It is obviously difficult to quantify such a complicated process, but it is often necessary to obtain estimates of the rate of biodegradation at a site. Two general rate laws have been proposed for biodegradation processes; the power rate law and the hyperbolic rate law.

2.7.2.1 Excess Substrate--

When the compound to be biodegraded, the substrate, is present in excess, the rate of increase of biomass can be approximated by the power rate law (EPA,1987):

$$\frac{dx}{dt} = k[x]^n \tag{44}$$

where

n = the order of the reaction (dimensionless)

k = biodegradation rate constant (1/sec when n = 1)

x = concentration of the biomass (g/l)

According to this equation, the rate of increase in biomass when there are large loadings (excess substrate) is therefore independent of the concentration of the organic compound to be degraded.

Alternatively, this equation can be written in terms of the substrate concentration, S:

$$-\frac{dS}{dt} = k[S]^n \tag{45}$$

where

S = concentration of the substrate (g/l)

First order kinetics are commonly assumed (n=1.0) if the media is homogeneous, or if the relationship between the concentration and the variables influencing it is not well understood. Integration of Equation 45, assuming that n=1, gives the following equation:

$$S = S_o e^{-kt} \tag{46}$$

where

S_o = the initial concentration of substrate (g/l)

The half-life of a chemical, $t_{1/2}$, which is the time at which one half of the initial concentration of substrate remains, can be determined from this equation, and is given by $t_{1/2} = 0.693/k$. The calculation of the half life is significant, because it gives some insight on the persistence of the chemical.

2.7.2.2 Limited Substrate--

If the amount of substrate available for biodegradation is limited, a hyperbolic rate law is recommended to describe the rate of change in concentration of the biomass (U.S. EPA, 1987a). This equation is based on Monod kinetics, and expresses the rate as a hyperbolic saturation function of the substrate concentration (Monod, 1942). The Monod kinetics rate equation can be written (ICF, 1984):

$$\frac{dx/dt}{x} = \frac{R_{max}\, S}{(K_s + S)} \tag{47}$$

where

R_{max} = maximum specific growth rate coefficient (for conditions when substrate is in excess) (1/sec)

K_s = substrate concentration at which the rate of substrate utilization is one-half of the maximum rate (g/l)

For the case when $S >> K_s$, the equation reduces to:

$$\frac{dx/dt}{x} = R_{max} \tag{48}$$

As before, when excess substrate is present, the rate is independent of the substrate concentration.

When $S << K_s$, the equation becomes:

$$\frac{dx/dt}{x} = \frac{R_{max}\, S}{K_s} \tag{49}$$

For intermediate values of S, Equation 47 should be used, since the biomass concentration is dependent on both R_{max} and on K_s (U.S. EPA, 1987a).

These equations describe conditions which are easily controlled in the laboratory, but which may be inapplicable to field conditions. For example, these equations assume a single substrate, although there may be several substrates in actual environmental situations. In the case of multiple substrates, the kinetics become more complex. Discussion of possible errors which can result from application of Monod kinetics to real situations is presented in Larson (1980).

2.7.3 Estimation of Parameters Used in Equations for Biological Decomposition

It is difficult to estimate the parameters used in equations which describe biodegradation. Although attempts have been made to correlate the biodegradability of a compound with its molecular characteristics, such as solubility, these generalizations are applicable only to the specific chemicals investigated, and are not recommended estimation techniques for other chemicals (Lyman et al., 1982). A significant amount of work is needed to validate the extension of these techniques to other chemicals and conditions.

A compilation of laboratory-derived biodegradation rate constants reported in the literature, along with the test conditions when available, is presented in Lyman et al. (1982). The tables include rate constants for several organic compounds in both aqueous environments and soils. However, since these constants were determined under laboratory conditions, they may be inapplicable to a field situation. Care should be taken in extrapolating these results to actual environmental situations.

2.7.4 Importance of Biological Decomposition as a Pathway for Removal of Contaminants from Sites

Biological decomposition is considered a primary pathway for removal of organics from surface impoundments, aerated and non-aerated aqueous treatment facilities, and land treatment facilities (U.S. EPA, 1987a). The relative importance of volatilization and biodegradation as pathways will be dependent on the tendency of the chemical in question to partition into the atmosphere; for highly volatile compounds, volatilization will be the predominant pathway and for low volatility compounds, biological decomposition will dominate. Biodegradation processes are considered secondary pathways in hazardous waste landfills, since the toxic properties of the water are thought to inhibit biological processes (Shen, 1981; U.S. EPA, 1987b).

2.8 OTHER PROCESSES

2.8.1 Photochemical Decomposition

Photochemical processes can be a pathway for removal of a contaminant from a site. Photolysis can occur in a direct sense, where the contaminant itself absorbs solar radiation and reacts, or in the case of sensitized photolysis, during which energy is transferred to the contaminant from another aqueous species which adsorbs the solar radiation. Lyman et al. (1982) presents guidelines for qualitatively determining which compounds will be photolytically reactive, and the types of reactions which might occur. They cover only direct photolysis; sensitized photolysis is dependent on the characteristics of the entire aqueous system, and is not discussed.

The rate constant for the direct photolysis rate equation, is dependent on the distribution of sunlight and its intensity, which is affected by the time of day, season, cloud cover and latitude. Typically a reference condition is stated, such as the light flux of photons per second corresponding to a cloudless yearly average at a latitude of 40° N (U.S. EPA,1987b). Data on rate constants are chemical-specific, and generally must be determined in the laboratory (Lyman et al., 1982). The rates of aqueous photochemical decomposition can be influenced by the properties of the water body as well, such as the suspended sediment content (Miller and Zepp, 1979a,b), depth of the water body, and presence of surfactants (Hautala, 1978). Furthermore, in order to estimate the rate of direct photolysis, the quantum yield for photolysis of the chemical must be known. Unfortunately, there are no methods for estimating this parameter based on the characteristics or properties of the chemical (Lyman et al., 1982).

Existing models for predicting photochemical reactivity in the environment are basically methods for calculating the net rate at which an aqueous solution containing an organic chemical absorbs light. A quantitative model for calculating the rate of absorption of light in aquatic environments can be found in a series of papers by Zepp and others (1976; 1977; 1978a,b,c; 1979; 1980).

2.8.2 Hydrolysis Processes

Hydrolysis is thought to be the most significant reaction of organic chemicals with water, and a potentially significant elimination pathway for many organic chemicals (Lyman et al., 1982). Hydrolysis of organic chemicals is thought to be a first-order rate process with respect to the concentration of the organic species (Faust and Gomaa, 1972; Wolfe et al., 1977; 1978). Methods for estimating the rate constant for the hydrolysis process are presented in Lyman. The rate of hydrolysis is dependent on temperature, pH, presence of organic solvents, ionic strength of the solution, and sediment content.

2.8.3 Oxidation/Reduction Processes

Organic compounds in aerobic environments may be oxidized by oxygen, hydroxyl radicals, or peroxyl radicals, which can reduce the concentration of the organic chemical in the system. Under anaerobic conditions, reduction reactions may take place. Rate equations for these processes are presented in U.S. EPA (1987b), but no methods are given for estimation of the rate constants used in the equations.

2.8.4 Hydroxyl Radical Reaction Processes

Reactions of organic chemicals in the atmosphere with hydroxyl radicals (OH^-) can decrease the concentration of the chemical. The rate of decrease of the chemical is dependent on a rate constant, and the concentration of the hydroxyl radical and chemical in the atmosphere. Values for rate constants can be found in Hendry and Kenley (1979). These rate constants are dependent on temperature. Typical concentrations of OH^- for different atmospheric conditions are tabulated in Lyman et al. (1982).

2.8.5 Importance of Other Processes as Pathways for Removal of Contaminants from Sites

Photodecomposition is considered to have a negligible affect on the removal of contaminants from aerated and non-aerated wastewater treatment plants, and land treatment facilities. It can be a significant pathway for shallow depths in surface impoundments. However, the rate of photochemical decomposition is negligible for depths greater than 3 meters (U.S. EPA, 1987b). Photodecomposition may also occur in land treatment facilities between the application of the waste to the soil and the tilling process, which incorporates it into the soil. However, the oil in which the chemical is typically suspended is semiopaque, and very little sunlight is thought to penetrate the oil. Therefore, the process of photodecomposition is thought to make only a small contribution to the removal of organics from a site (U.S. EPA, 1987b).

Hydrolysis processes are generally thought to be of secondary importance in the removal of organics from surface impoundments and aerated and non-aerated wastewater treatment facilities. Hydrolysis is considered negligible at land treatment sites. Oxidation/reduction and hydroxyl radical reactions are considered to be insignificant pathways for the removal of organic chemicals from a hazardous waste treatment facility (U.S. EPA, 1987b).

None of the emission models described in the following chapters deal with photochemical decomposition, oxidation/reduction, and hydroxyl radical reactions or hydrolysis explicitly. One reason for this is the lack of available data on these processes upon which to develop the model relationships (U.S. EPA, 1987b). However, some models include these processes, along with biodegradation, in an overall degradation rate term.

The other reason photochemical decomposition, oxidation/reduction and hydroxyl radical reactions or hydrolysis are not commonly included in the models is that they are generally considered relatively insignificant as pathways in comparison to the processes of volatilization, biodegradation and adsorption. Most of the models are limited to one or more of these primary pathways. However, processes other than volatilization, biodegradation and adsorption may be important for individual chemicals in a given site. For example, some chemicals are particularly sensitive to photochemical decomposition. In these cases, the accuracy of the emission models will be improved if these other pathways for removal of a contaminant are considered.

SECTION 3

DESCRIPTION OF BIOREMEDIATION PROCESSES

3.1 INTRODUCTION

All bioremediation processes rely on the activity of microorganisms to consume or transform organic pollutants. The general characteristics of these microorganisms can be used to group the various bioremediation processes.

One broad classification is based on the electron acceptor used by the microorganisms. When oxygen is present and is used as the electron acceptor, a process is termed aerobic. If oxygen is absent, the process is anaerobic. Aerobic bioremediation processes are the most common of the two. Eckenfelder et al. (1989) compare aerobic and anaerobic treatment systems. Their comparison is summarized in Table 3-1. The authors explain that aerobic growth processes are more efficient, resulting in higher removal efficiency, sludge production, and energy requirements. Aerobic processes also require less start-up time and less control of environmental conditions. However, anaerobic processes can accept higher waste loading than aerobic processes. Thus, they are successfully used in the pretreatment of high-strength wastes. Some chemicals can only be degraded by one of the two processes.

Another broad classification is based on the growth environment of the microorganisms. The microorganisms can grow within a primarily aqueous environment or within a solid matrix, such as soil or composting material. The aqueous bioremediation processes can be further grouped as either suspended-growth or fixed-film systems. The soils-related bioremediation processes include soil-incorporation techniques and in-situ remediation processes.

In suspended-growth systems, microorganisms grow unattached to any solid, suspended in an aqueous medium. Most suspended-growth systems are aerobic and their design results in better aeration and mixing than is achieved in fixed-film systems. Thus they have higher removal efficiencies. Also, their operation is more flexible and they are less sensitive to climatic changes than fixed-film systems.

In fixed-film systems, degradation occurs by means of a biofilm attached to a solid surface past which wastewater flows. Fixed-film systems usually require less energy, are easier to operate, and are more stable under shock loading than suspended-growth systems. They also require less land because they can handle higher waste loads.

TABLE 3-1. COMPARISON OF ANAEROBIC AND AEROBIC TREATMENTS (from Eckenfelder et al., 1989)

Parameter	Anaerobic	Aerobic
Energy requirements	Low	High
Degree of treatment	Moderate (60-90%)	High (95% +)
Sludge production	Low	High
Process stability (to toxic compounds and load changes)	Low to moderate	Moderate to high
Startup time	2 to 4 months	2 to 4 weeks
Nutrient requirements	Low	High for certain industrial wastes
Odor	Potential odor problems	Less opportunity for odors
Alkalinity requirements	High for certain industrial wastes	Low
Biogas production	Yes (net benefit is contingent on the need for reactor heating)	No

Biofilms are usually modeled as shown in Figure 3.1. The concentration of the substrate in the bulk liquid, C, diffuses through a stagnant liquid film at the biofilm interface. The concentration at the interface, C_f, is less than in the bulk liquid. Within the biofilm, diffusion and biological reactions cause the concentration, C_b, to decrease with increasing depth.

Soil-incorporation techniques rely on microorganisms in a soil or composting material to degrade added contaminated solids, liquids, or gases under controlled conditions. In-situ remediation processes minimize disturbance to the environment. At contaminated sites, techniques are used to enhance the growth of naturally-occurring microbes in either the saturated or unsaturated zones of the subsurface.

A list of specific bioremediation processes which are currently in use or in advanced stages of research is presented in Figure 3.2. In the list, the specific processes are grouped under the four general headings discussed above. Each process is described briefly in the sections which follow. Whenever possible, the descriptions include information on the types of contaminants treated by the process, the potential for air emissions from the individual components of the bioremediation process, including data on emissions when known, and the relative advantages and disadvantages of using the process.

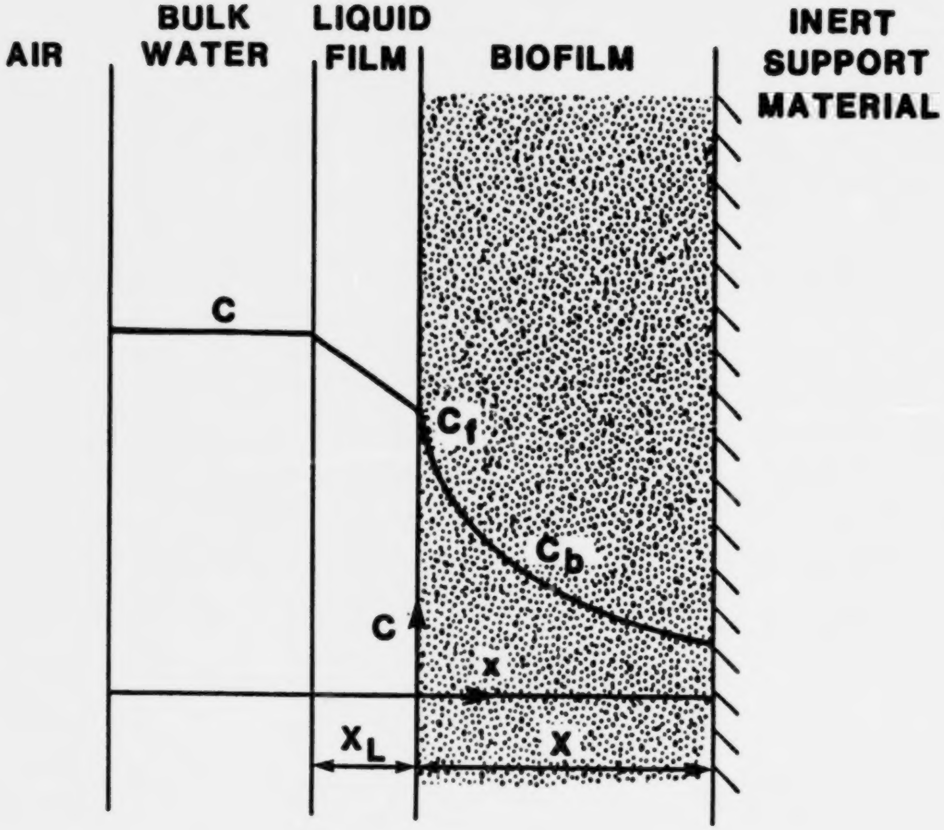
AIR
BULK WATER
LIQUID FILM
BIOFILM
INERT SUPPORT MATERIAL
C
C_f
C_b
C
x
X_L
X

Figure 3.1. Typical substrate concentration profile for a fixed-film system (from Sarner, 1986).

I. Suspended-Growth Systems

   A. Activated Sludge
   B. Powdered Activated Carbon Treatment
   C. Sequencing Batch Reactors
   D. Surface Impoundments
      1. Lagoons (aerobic, facultative, anaerobic)
      2. Waste Stabilization Ponds
      3. Aerated Stabilization Basins

II. Fixed-Film Systems

   A. Trickling Filters
      1. Trickling-Filter/Solids-Contact Treatment
   B. Rotating Biological Contactors
   C. Submerged Packed Beds
   D. Fluidized Beds
      1. Biological Activated Carbon

III. Soil Incorporation

   A. Land Treatment (Landfarming)
   B. Composting
   C. Soil Filter Beds (Biofilters)

IV. In-Situ Bioremediation

   A. Saturated
      1. Pump-and-Treat
      2. Enhancement by Other Means
   B. Unsaturated
      1. Enhancement

V. Related Physical Remediation Processes

   A. Soil Venting (Vapor Extraction)
   B. Soil Washing

Figure 3.2 Bioremediation processes currently in use or under investigation.

3.2 SUSPENDED-GROWTH SYSTEMS

3.2.1 Activated Sludge

The activated-sludge process is the most common treatment process for municipal wastewater. Traditionally, plants have been operated to remove organics measured as biological oxygen demand (BOD), suspended solids and inorganic nutrients. However, the activated-sludge process is also being used successfully to treat specific industrial wastes and water contaminated by other treatment processes (e.g., soil washing). The overall performance of an activated-sludge facility is affected by the types of organics present in the wastewater and the degree of acclimation of the microorganisms in the sludge. Aliphatic and aromatic organics, as well as halogenated hydrocarbons have been treated by this process (PEI Associates, 1988).

An activated-sludge facility consists of three main components and operates as a continuous-flow system (Figure 3.3). The influent enters either one or a series of aeration tanks in parallel, where it contacts suspended microorganisms and is biodegraded. Many conventional municipal treatment plants have rectangular, open aeration basins and operate under plug-flow conditions. Completely-mixed basins have become more common in recent years, particularly at facilities designed to treat hazardous waste. The aeration tank is either mechanically agitated by means of surface aerators or sparged with air by means of a diffused-air system. The agitation improves mixing and helps oxygen transfer to the liquid. The retention time in the aeration basin, which is on the order of hours, can be controlled to achieve a desired level of biodegradation of organics. A mixture of biomass and liquid flows from the aeration basin to a settling tank for clarification. The effluent leaving the settling tank can be further treated by means of other processes or discharged to the environment, depending on case-specific requirements. A sludge recycling system returns most of the settled sludge to the aeration tank. Recycling the sludge allows an acclimated biomass to develop over time and maintains a constant concentration of biomass in the tank. The excess sludge is removed from the settling tank on a continuous basis for treatment and disposal. Typical design parameters for activated-sludge units are given in Eckenfelder et al. (1984).

In addition to biodegradation, the mechanisms affecting the fate of organics during the activated-sludge process are adsorption, passive volatilization from the liquid surface, and stripping at the dispersed gas/water interface of spray droplets in mechanically-mixed systems or of air bubbles in sparged systems. Stripping is a more significant source of emissions than passive volatilization, because the total surface area, across which transfer of organics can occur, increases during aeration. Roberts et al. (1984) indicate that surface aeration strips volatile organics more effectively than bubble aeration does. This is because the rate of stripping is proportional to the gradient between the concentration in the liquid and the gaseous phases. Air bubbles in the liquid become at least partially saturated with the volatile organics as they rise through the tank, while the concentration of the organics in the air in contact with the spray droplets is very low and is often assumed to be zero (Barton, 1987).

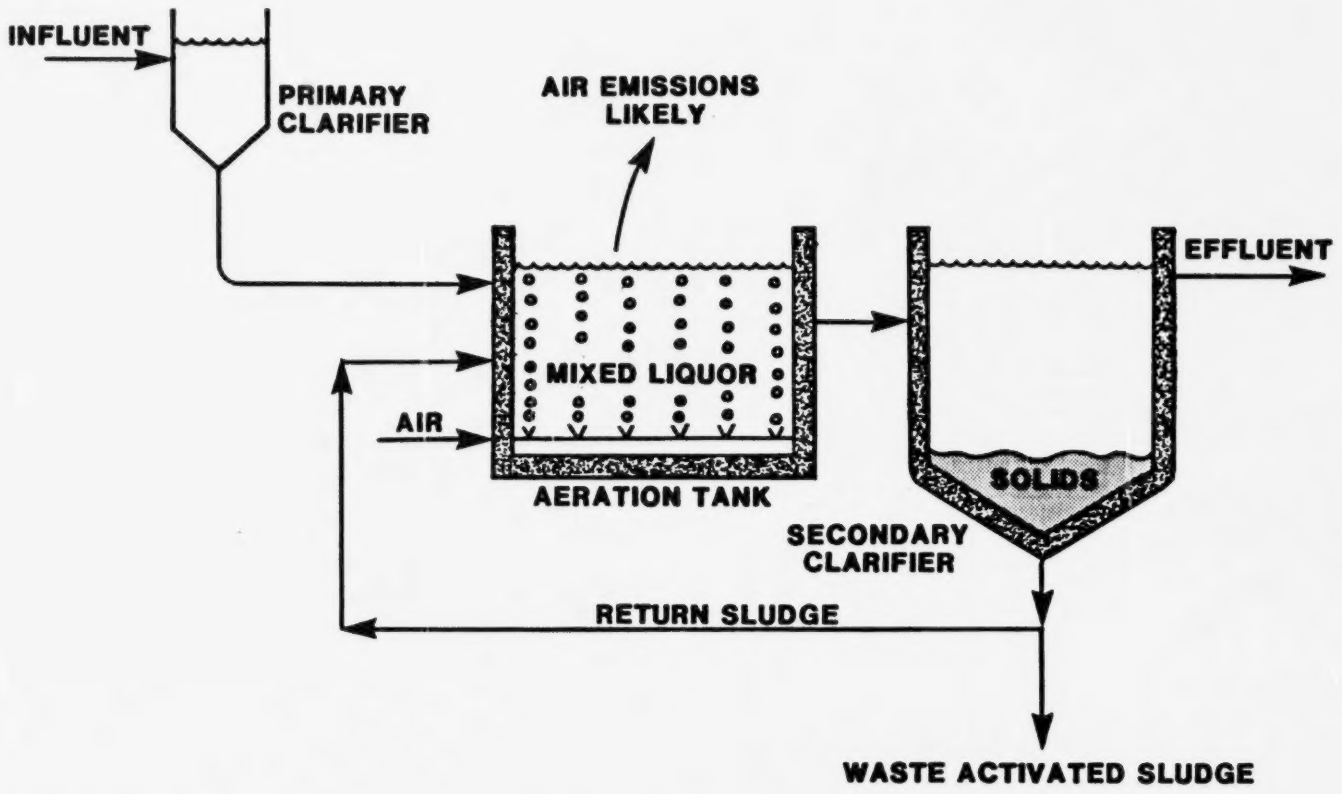
INFLUENT
PRIMARY CLARIFIER
AIR EMISSIONS LIKELY
EFFLUENT
MIXED LIQUOR
AIR
AERATION TANK
SOLIDS
SECONDARY CLARIFIER
RETURN SLUDGE
WASTE ACTIVATED SLUDGE

Figure 3.3. The diffused-air activated-sludge process (from Blackburn et al., 1984).

Significant air emissions of volatile and semi-volatile organics can occur from the aeration tank. Kincannon et al. (1983) found that nitrogen compounds, phenols, and oxygenated compounds were removed from an aeration tank chiefly by biodegradation. Halogenated hydrocarbons were removed mainly by stripping, and aromatics were removed by a combination of the two mechanisms. Melcer et al. (1989) found that stripping was the main mechanism for removal of seven chlorinated organic compounds (VOCs) from an aeration basin, whereas biological removal was most significant for 15 non-chlorinated VOCs. Others have shown that approximately 20% of total influent VOCs are volatilized or stripped from steady-state activated-sludge experiments (Namkung and Rittmann, 1989). Stripping and passive volatilization may be the dominant removal mechanisms for an organic to which the biomass in the system is not acclimated (Melcer, 1986). Some volatilization will occur from the quiescent surface of the settling tank. Relative to those from the aeration basin, however, emissions from the settling tank should be small.

Adsorption is generally considered of minor importance in the activated-sludge process. The work of several researchers indicates that volatile organics do not significantly adsorb to waste sludge (Hannah, 1986; Kincannon and Stover, 1981). Relatively non-volatile organics, such as polycyclic aromatic hydrocarbons are adsorbed to the sludge, however (Melcer, 1986). Barton (1987) found that sorption is significant for chemicals with an octanol-water partition coefficient greater than five liter/gram.

Some of the commonly-listed disadvantages of the activated-sludge process include the high capital investment required, high energy costs, the lengthy start-up time, and sensitivity to toxic and hydraulic shocks. On the other hand, the system can handle high organic loads using relatively short retention times, and can be controlled to achieve various degrees of treatment. Finally, the widespread use of activated-sludge facilities means the process has been well researched and documented.

3.2.2 Powdered Activated Carbon Treatment (PACT^{tm})

Powdered activated-carbon treatment is a relatively new process in which powdered activated carbon is added to the aeration basin of an activated-sludge facility (Figure 3.4). The physical adsorption properties of the powdered activated carbon, (ranging in concentration from 1000 to 10,000 mg/liter in the aeration basin) enhances removal of hazardous wastes. Full-scale PACT systems have been reported in the literature (PEI Associates, 1989).

A number of advantages have been reported for this combined physical/biological process. These include the removal of non-biodegradable organics, reduced emission of organics to the air, particularly during the period of acclimation, better settling properties of the biomass/powdered activated-carbon sludge, and protection of the microbial population from toxic shocks. In addition, the powdered activated carbon helps reduce effluent concentrations of organics during an acclimation period. Some evidence also exists for the ability of microorganisms to bioregenerate the powdered activated carbon during periods of low organic loading (Schultz and Keinath,

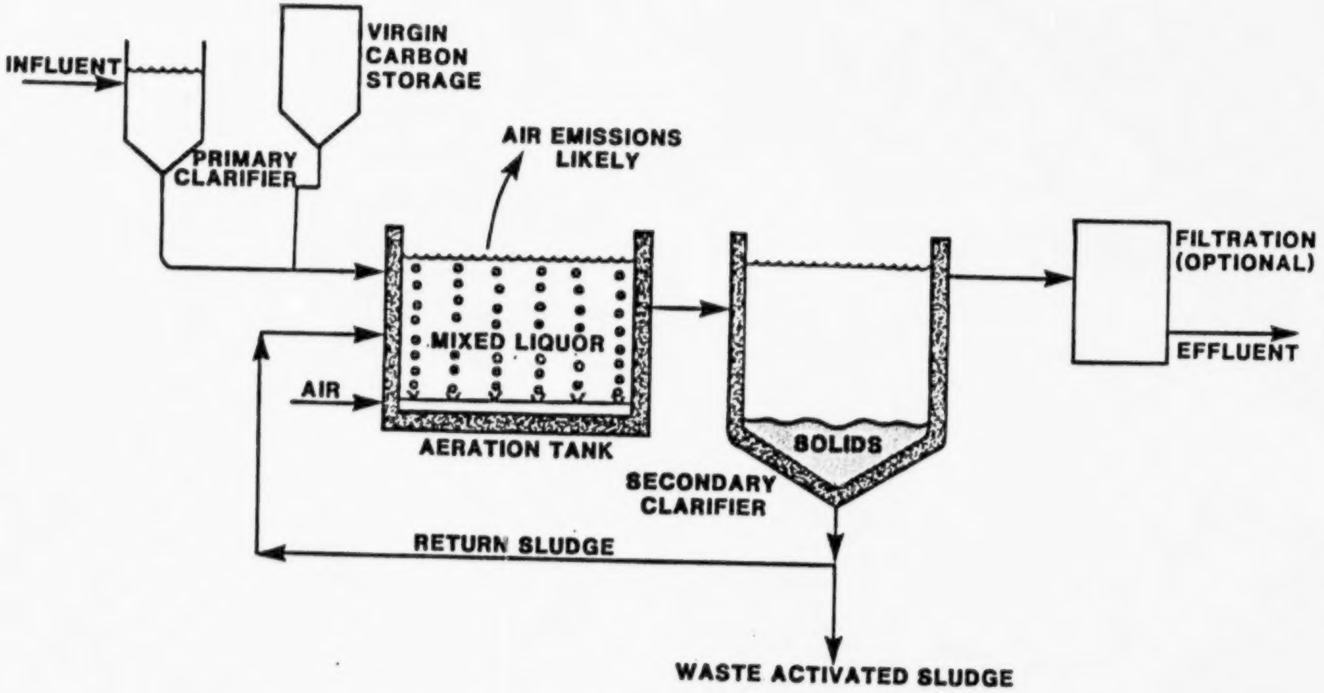
INFLUENT
VIRGIN CARBON STORAGE
PRIMARY CLARIFIER
AIR EMISSIONS LIKELY
MIXED LIQUOR
AIR
AERATION TANK
SOLIDS
SECONDARY CLARIFIER
FILTRATION (OPTIONAL)
EFFLUENT
RETURN SLUDGE
WASTE ACTIVATED SLUDGE

Figure 3.4. The diffused-air powdered activated carbon process (from Blackburn et al., 1984 and Dietrich et al., 1988).

1984). The major disadvantage of the system is cost, which may be greater than those of other bioremediation processes (PEI Associates, 1988).

Just as for the conventional activated-sludge process, emissions of VOCs to the air are likely to occur from the aeration basin, and possibly from the settling tank. Data have not yet been located on the magnitude of those emissions. Qualitatively, it can be assumed to be smaller than for the activated-sludge process.

3.2.3 Sequencing Batch Reactors

The sequencing batch reactor technology is similar to the more widely used activated-sludge process. The main difference is that the five-step treatment cycle is carried out in one tank in batch mode (Figure 3.5). Sequencing batch reactor technology predates that of the continuous-flow activated-sludge process, but was little used for many years. Recent advances in equipment have caused revived interest in sequencing batch reactors, but their use is still in its infancy (Arora et al., 1985). Several full-scale facilities are operating in this country, treating both municipal wastes and hazardous waste leachates (PEI Associates, 1988).

Ying et al. (1986) describe the five-step cycle of the aerobic sequencing batch reactor process as follows: 1) FILL--wastewater flows into the tank, which contains some of the activated sludge from a previous cycle. Aeration may or may not occur during this step. 2) REACT--aeration and mixing occur to stimulate aerobic biological degradation of the organics, 3) SETTLE--aeration and mixing are stopped to allow clarification, 4) DRAW--the treated and clarified wastewater is withdrawn from the reactor for discharge or further treatment, and 5) IDLE--the settled biomass remains idle in the tank until another cycle begins. Most sequencing batch reactors make use of aerobic biological processes. Recently, however, anaerobic systems have also been developed. To provide continuous treatment of wastes, either a multi-tank configuration of reactors or a single reactor connected with storage tanks are needed.

Significant emissions of volatile organics to the air from sequencing batch reactors can occur during the FILL and REACT steps, when aeration and mixing are greatest. Ying et al. (1986) found that air stripping was the predominant removal mechanism for the aromatic and straight-chained chlorinated hydrocarbons in a landfill leachate treated in an aerobic reactor. The stripped volatiles accounted for approximately 5% of the total organic carbon in the wastewater. Kincannon et al. (1983) indicate that organics which are strippable are more likely to be stripped from batch reactors than from completely-mixed reactors, such as activated-sludge aeration tanks. The authors suggest that the higher concentrations of priority pollutants often found in batch reactors may inhibit biodegradation to a greater extent than in activated-sludge tanks, thus causing the difference. As is the case for the activated-sludge process, adsorption of organics onto the biomass is not considered an important removal mechanism.

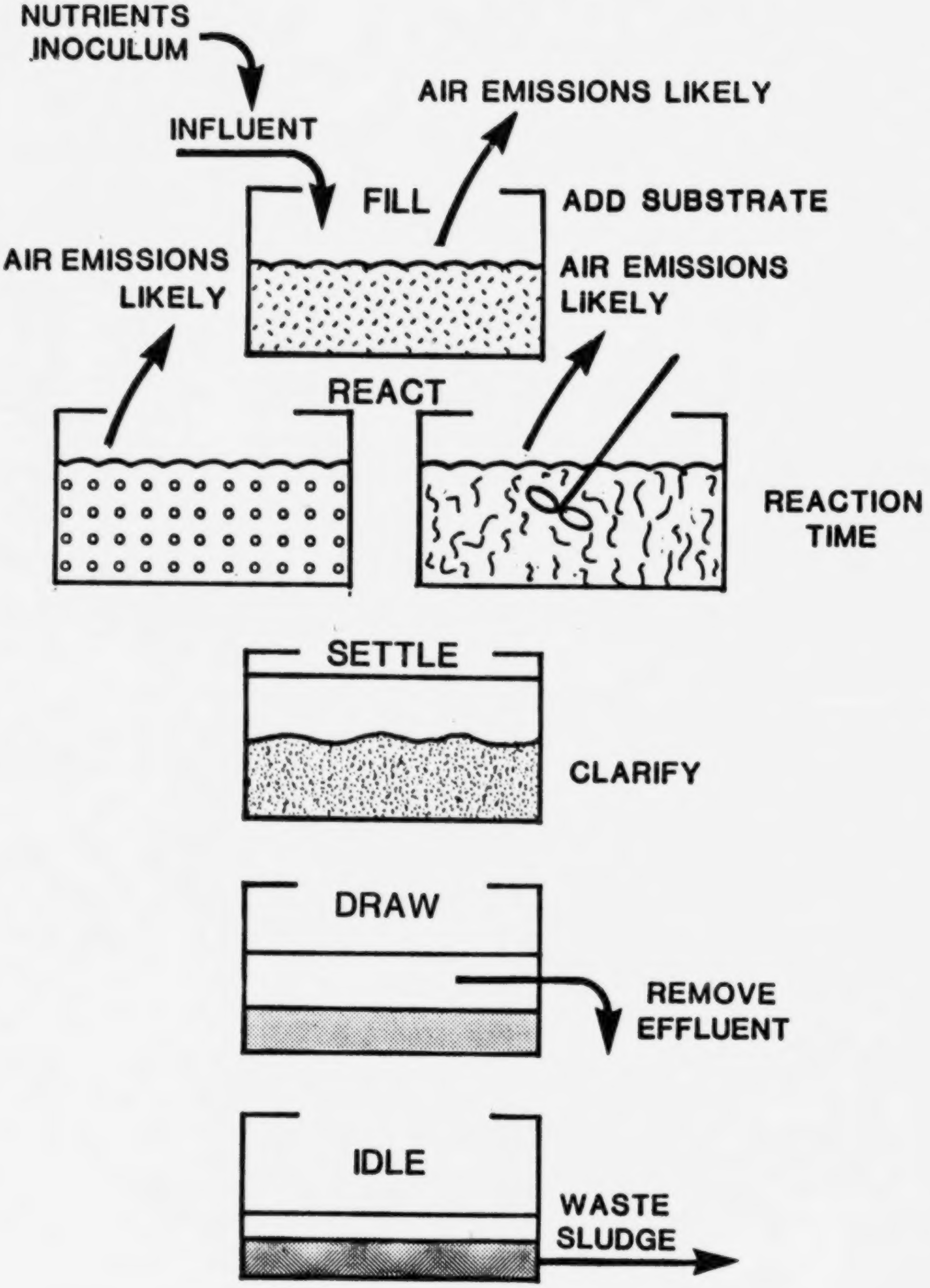
NUTRIENTS
INOCULUM
INFLUENT
AIR EMISSIONS LIKELY
FILL
ADD SUBSTRATE
AIR EMISSIONS LIKELY
AIR EMISSIONS LIKELY
REACT
REACTION TIME
SETTLE
CLARIFY
DRAW
REMOVE EFFLUENT
IDLE
WASTE SLUDGE

Figure 3.5. The five-step sequencing batch reactor process (from PEI Associates, Inc., 1988).

Sequencing batch reactors have been shown to handle greater flows and higher loads with better effluent quality than activated-sludge facilities (Orhon et al., 1986). Also, they provide greater flexibility in operation and can be used intermittently when waste generation is low. Because only one tank is needed, capital and space requirements are less than for the activated-sludge process. The operation of sequencing batch reactors does require a better control strategy than for activated sludge, however (Orhon et al., 1986). Also, the system does not tolerate rapid changes in temperature. As is the case for activated sludge, the excess sludge, which may contain toxic organics and heavy metals, needs to be treated and disposed of.

3.2.4 Surface Impoundments

The use of ponds to accumulate and treat organic matter from farms is an ancient practice (Vuillot and Boutin, 1987). Waste stabilization ponds, a type of surface impoundment which relies only on natural processes for aeration, are still commonly used to treat domestic wastewater. Mechanically-aerated lagoons (Figure 3.6), another type of surface impoundment, have been used to successfully treat leachate from sanitary landfills.

There are three main classes of surface impoundments: aerobic, facultative, and anaerobic lagoons. Aerobic lagoons can be further categorized as either the mechanically-aerated lagoons or the waste stabilization ponds mentioned above. A special type of mechanically-aerated lagoon, known as an aerated stabilization basin, is used extensively in the pulp and paper industry. While it is actually a partially mixed, facultative system (Sackellares et al., 1987), it is predominantly aerobic and is often assumed to be fairly well mixed (Barton, personal communication). In facultative lagoons, which are the most common type of lagoon, aerobic biological activity occurs near the surface and anaerobic conditions exist near the bottom. Few facultative and no anaerobic lagoons are mechanically aerated. Therefore, they tend to be easier and less expensive to operate than mechanically-aerated lagoons. They tend to produce foul odors, however, and can fail to provide complete degradation of organics (Lee et al., 1988).

Typical design parameters, as compiled in EPA (1987b), for surface impoundments are presented in Table 3-2. The authors point out that large variations exist between facilities and even for the same facility over time. All three main classes of surface impoundments have some common characteristics. They have large space requirements and long retention times (on the order of weeks instead of the hours required for activated sludge). Because they can handle only low-strength wastes, they are best used as part of a treatment sequence, using different processes (PEI Associates, 1988). A disadvantage relative to other suspended-growth processes is that the biomass in the effluent is not recycled and no clarification of the effluent occurs. Their biggest advantage is that they require less energy and supervision than most other processes, and thus provide a simple and inexpensive form of treatment. Removal efficiencies of surface impoundments range from 60-90% (Lee et al., 1988). Removal efficiency is influenced both by biological transformations and the hydraulic transport process in a pond (Polprasert and Bhattarai, 1985).

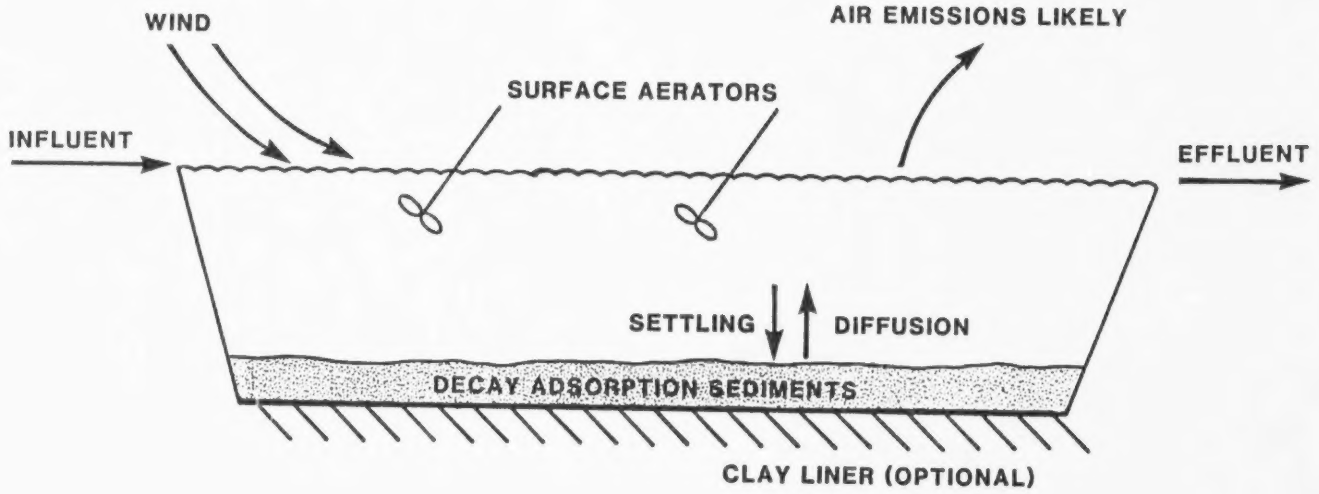
WIND
AIR EMISSIONS LIKELY
SURFACE AERATORS
INFLUENT
EFFLUENT
SETTLING
DIFFUSION
DECAY ADSORPTION SEDIMENTS
CLAY LINER (OPTIONAL)

Figure 3.6. A typical aerated surface impoundment.

TABLE 3-2. SURFACE IMPOUNDMENTS DESIGNED FOR BIODEGRADATION (from EPA, 1987)

Type	Application	Typical daily loading, kg $BOD_5/m^3 \cdot day$	Retention time, d	Typical depth, m	Suspended solids, g/L
Facultative	Raw municipal wastewater Effluent from primary treatment, tricking filters, aerated ponds, or anaerobic ponds	0.0011-0.0034[a]	25-180	1.2-2.5	0.11-0.40
Aerated	Industrial wastes Overloaded facultative ponds Situations where limited land area is available	0.008-0.32	7-20	2-6	0.26-0.30
Aerobic	Generally used to treat effluent from other processes, produces effluent low in soluble BOD_5 and high in algae solids	0.021-0.043[b]	10-40	0.3-0.45	0.14-0.34
Anaerobic	Industrial wastes	0.16-0.80	20-50	2.5-5	0.08-0.16

[a] Based on a typical depth of 2 m.
[b] Based on a typical depth of 0.4 m.

Volatilization of organics from surface impoundments can be significant. Thibodeaux et al. (1982) measured total hydrocarbon fluxes from aerated stabilization basins during field testing of a sampling method. The flux rate was roughly 23 lb/acre-day for the conditions under which the testing occurred. Emissions from a quiescent surface would be somewhat less. Thibodeaux et al. (1982) found that the emission of methanol increased with increases in compound concentration in the water, wind speed and water temperature.

Shen and Sewell (1988) state that surface impoundments are the largest source of organic compound emissions of all hazardous waste treatment, storage, and disposal facilities, accounting for almost half the total. According to Shen and Sewell (1988) emissions from surface impoundments used for treatment of wastes amount to approximately 376,000 metric tons per year.

Surrounding impoundments with fences to block the wind and covering impoundments with an immiscible oil are two suggested methods for reducing emissions from surface impoundments (Springer et al., 1985). An oil film can not be used for impoundments in which aerobic biological activity is desired, however, because the oil film inhibits oxygen transfer into the water.

3.3 FIXED-FILM SYSTEMS

3.3.1 Trickling Filters

A trickling filter (Figure 3.7), the original plug-flow, fixed-film process, relies on the activity of microorganisms in an attached biofilm to degrade organics. The organics diffuse into the biofilm from wastewater, which is sprayed onto the top of a support medium. The wastewater flows over the biofilm as it trickles through the system. Retention time and flow characteristics determine the thickness of the biofilm. During the course of operation, excess biofilm sloughs off and must be separated from the effluent, requiring a clarifier as part of the treatment system.

Rocks were the original support medium for the biofilm. The height of rock filters is typically one to two meters. In recent years, plastic media designed to maximize the biofilm surface area have been developed. Plastic media tower heights can be one to twelve meters because of the high void space and low weight (Logan et al., 1987). Normally, air is supplied to trickling filters through natural drafts. Some deep plastic filters require the use of compressed air to supply forced drafts (Tchobanoglous and Schroeder, 1985).

Aerobic trickling filters can handle only low organic loadings. Standard trickling filters can accept organic loadings of 0.11 to 0.37 $kg/m^3/day$ and hydraulic loadings of 0.94 to 3.74 $m^3/m^2/day$. They achieve a 60-85% reduction in BOD (Lee et al., 1988). Therefore, they are often used as a polishing process for other treatment systems or as a pretreatment process. Also, anaerobic trickling filters have been developed which can handle higher organic loads.

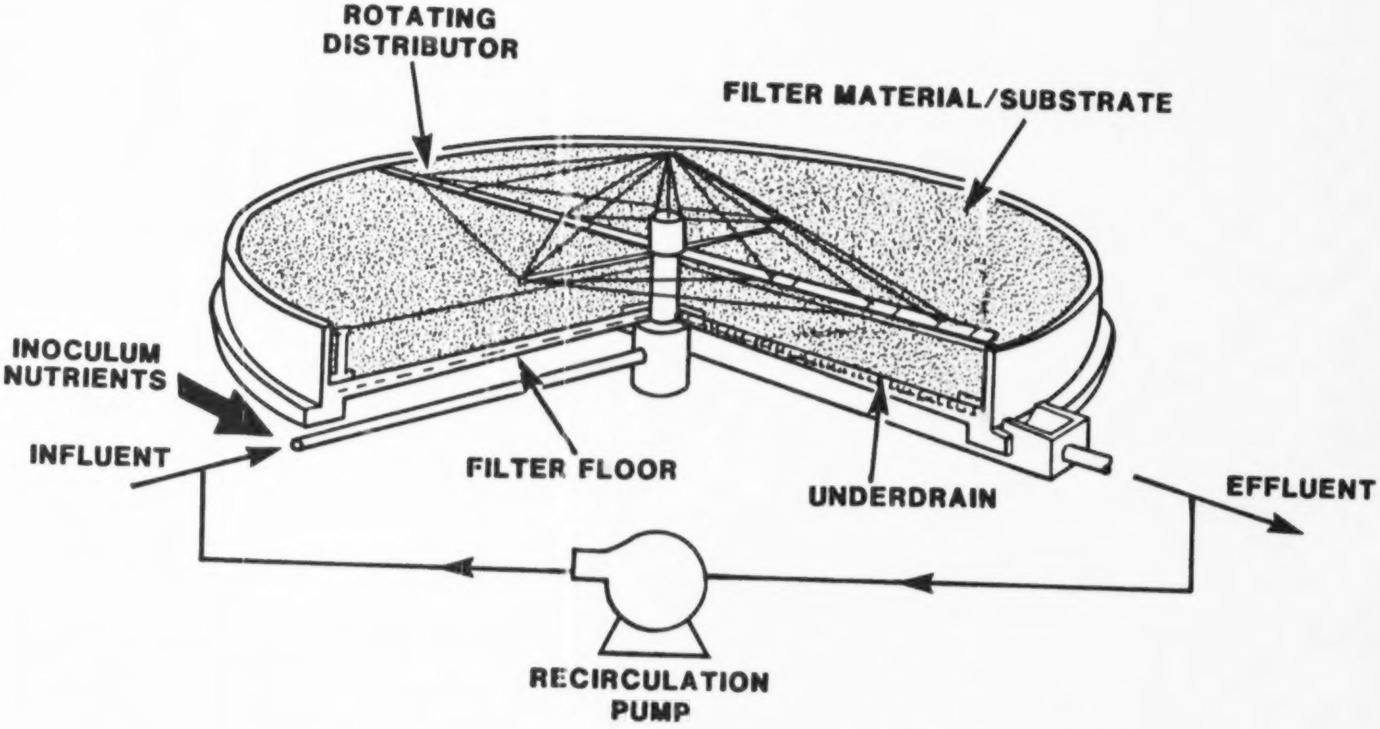
ROTATING DISTRIBUTOR
FILTER MATERIAL/SUBSTRATE
INOCULUM NUTRIENTS
INFLUENT
FILTER FLOOR
UNDERDRAIN
EFFLUENT
RECIRCULATION PUMP

Figure 3.7. The trickling-filter process (from Metcalf and Eddy, Inc., 1979).

Operation efficiency can be increased by recycling the effluent. Effluent recycling increases shearing and helps prevent clogging. It also damps out the effect of flow variations and improves organic distribution through the system (Tchobanoglous and Schroeder, 1985).

Trickling filters develop a more diverse microbial population than suspended-growth systems do. In addition, distinct populations develop in different sections of the tank. As a result, multi-stage treatment occurs in the same system. The biofilm can tolerate variations in organic loading, but if a toxic shock kills the biofilm, recovery is slow. A disadvantage of trickling filters is that they can only handle wastes with less than 1% solids (PEI Associates, 1988).

Little information is available on the use of trickling filters to treat hazardous chemicals. Hannah et al. (1988) treated municipal wastewater spiked with 21 priority pollutants in a pilot-scale trickling filter. Overall removal of the volatiles was greater than 91%. The authors noted that stripping was the primary removal mechanism for volatiles. For semi-volatiles, the chief removal mechanism was biological activity. No data have been located on the magnitude of air emissions from full-scale trickling filters.

3.3.1.1 Trickling-Filter/Solids-Contact Process--

This innovative technology, which combines physical and biological processes, is described in a paper by Matasci et al. (1986) and is shown in Figure 3.8. Most of the following information is taken from that paper.

The trickling-filter/solids-contact process was developed in 1979 and is gaining in popularity. It produces better quality effluent than trickling filters and is economical and reliable. In the process, a trickling filter is used to degrade soluble BOD. The effluent from the trickling filter is further treated in an aerobic solids-contact tank. The main purpose of the tank is to decrease particulate BOD by means of flocculation. It also is able to remove approximately 75% of the soluble BOD which remains after trickling-filter treatment. Thus, the solids-contact tank serves as a polishing unit with a low retention time. Flocculation is initiated when the effluent contacts biological solids. The system also has two clarification tanks in which the flocculated solids settle. Some of the settled solids are recycled to the solids-contact tank.

No specific information is available on air emissions from this process. The trickling filter is a likely source of emissions, as was discussed earlier. The solids-contact tank is completely-mixed and aerated, so its operation is similar to that of an aeration basin at an activated-sludge facility, only the concentration of organics is lower. Thus, the magnitude of emissions should also be smaller. Some emission from the clarifiers is also possible, but not likely to be significant. The first clarifier is stirred mildly and the second has a quiescent surface.

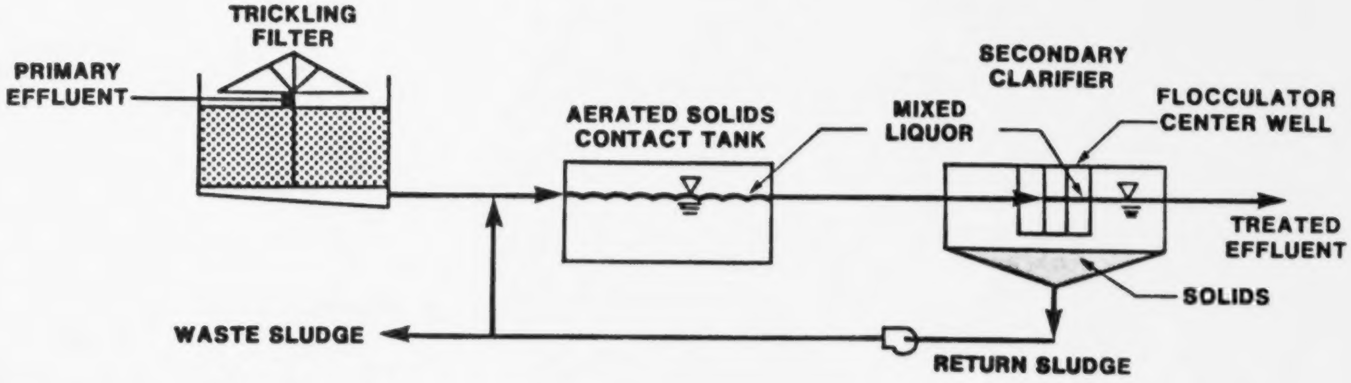
TRICKLING FILTER
PRIMARY EFFLUENT
AERATED SOLIDS CONTACT TANK
MIXED LIQUOR
SECONDARY CLARIFIER
FLOCCULATOR CENTER WELL
TREATED EFFLUENT
SOLIDS
WASTE SLUDGE
RETURN SLUDGE

Figure 3.8. The trickling-filter/solids-contact process (from Matasci et al., 1986).

3.3.2 Rotating Biological Contactors

Rotating biological contactors (RBC) were developed in the 1920's, but were used little until the 1960's. Their use is increasing now, primarily in the treatment of domestic wastewater, but also in the treatment of landfill leachate and petroleum-refinery wastes. Lee et al. (1988) state that RBC systems are as effective as the activated-sludge process in removing organics, yet easier and less expensive to use.

An aerobic RBC system (Figure 3.9) consists of a biofilm growing on closely-spaced, corrugated plastic disks attached to a horizontal shaft. The disks are partially submerged (usually 40%) and rotated through wastewater at one to two revolutions per minute. The rotation aerates the biofilm, which is alternatively exposed to air and contaminate. The ideal biofilm thickness is 2-4 mm (PEI Associates, 1988). The excess biofilm sloughs off the disks, requiring the use of a clarifier.

RBC systems can be run in either batch or continuous-flow mode and either aerobically or anaerobically. Their efficiency is controlled by the hydraulic retention time and the rotation speed of the disks. Like all fixed-film systems, they require a fairly long start-up time while the biofilm grows, and because they are sensitive to temperature, shock loading, and extreme dryness, they are only moderately reliable (Lee et al., 1988).

In addition to requiring less energy than many aerated systems, RBC systems have several other advantages. They require little land. Also, they can be covered to control climate and emissions and can withstand organic and hydraulic surges. Anaerobic systems can handle medium- to high-strength wastes, while producing fewer biological solids.

No data have been located on emissions from RBC systems. Emissions are expected to occur from the surface of the wastewater, in which the disks are suspended. Also, some volatilization may occur from the thin film of water covering the biofilm when it is out of the water.

3.3.3 Submerged Packed Beds

Submerged packed beds are a recent technology. Aerobic systems have been used successfully to treat groundwater contaminated with ketone (Sklandany et al., 1987) and with phenols and polynuclear aromatics (Chresand and Martinson, 1988). Lee and Stensel (1986) report 90% removal of BOD with a loading of 3-5 kg/m^3-day and a hydraulic retention time of one hour. Anaerobic submerged packed beds are also used to treat hazardous waste. They have been used to treat strong waste at BOD levels greater than 2000 mg/liter. Sikkema et al. (1988) report that 84 to 99% of specific volatile priority pollutants were biodegraded in an anaerobic packed bed system, operating under steady-state conditions.

In the process, a stationary biofilm grows on a fixed bed (e.g., fired clay). Unlike a trickling-filter system, the biofilm is completely submerged in the wastewater, which is held at a constant level in the treatment tank. For aerobic systems, air is sparged up through the bed. A compartmental design is

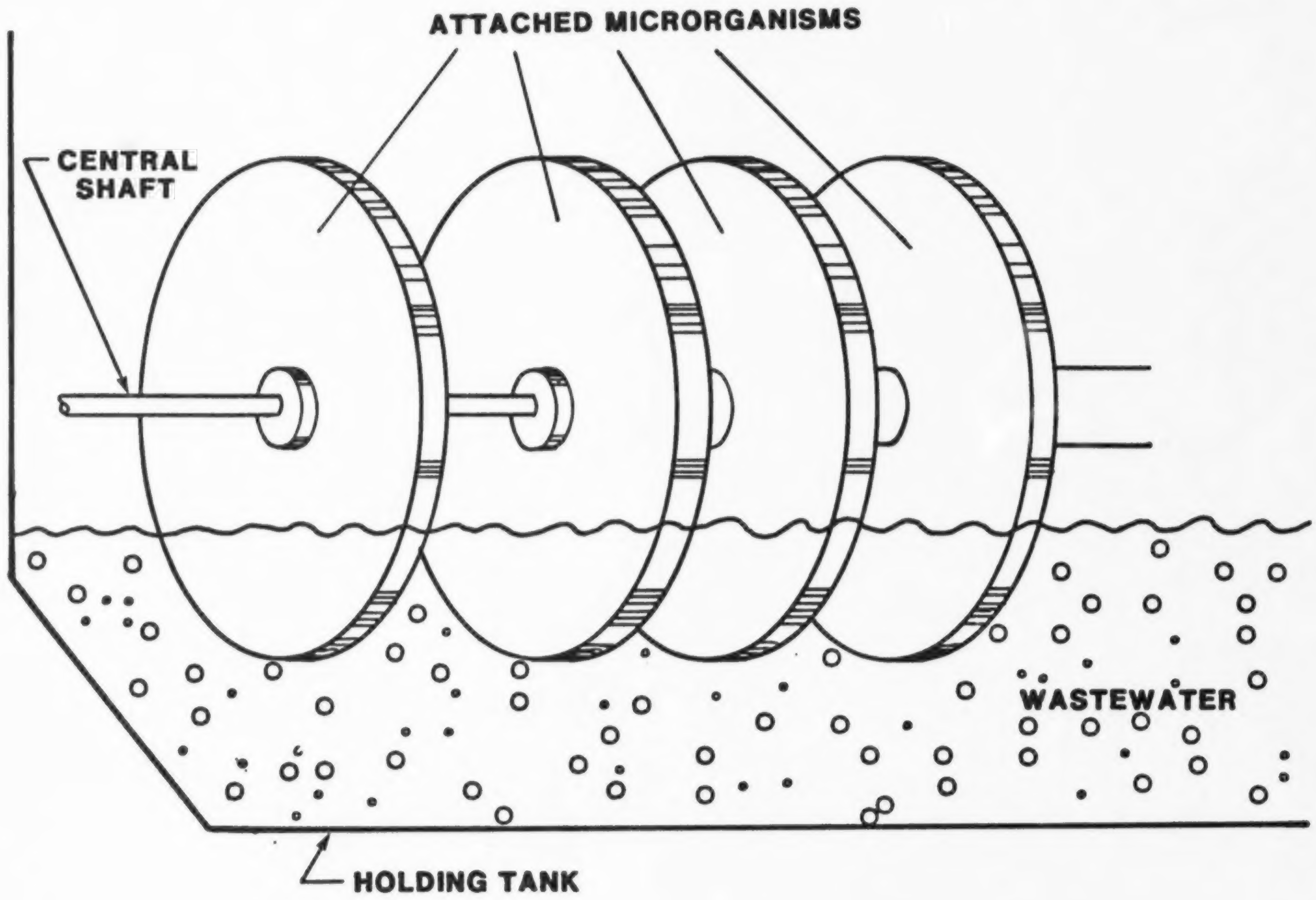
ATTACHED MICROORGANISMS
CENTRAL SHAFT
WASTEWATER
HOLDING TANK

Figure 3.9. An aerobic rotating biological contactor.

often used to prevent hydraulic short-circuiting of the primary effluent as it flows in the system. The diffused air helps maintain a mixed liquid and also shears excess biofilm off the medium. The system can then be periodically backwashed to remove the excess biomass (Hamoda and Abd-el-Bary, 1987). A representative submerged packed bed is shown in Figure 3.10.

Submerged packed beds require less energy than fluidized beds and avoid the climate problems associated with rotating biological contactors. They also require little space.

No information has been located on air emissions from submerged packed beds. Because they are sparged, emissions are likely to occur from aerobic systems. Emissions can be controlled if the reactors are covered.

3.3.4 Fluidized Beds (Expanded Beds)

In fluidized-bed reactors (Figure 3.11), solid material, which is colonized by microorganisms, is suspended by water flowing upward through the tank. The solid material is either inert (e.g., sand, coal, or plastic) or active (i.e., granular activated carbon). Both aerobic and anaerobic types of fluidized beds are in use or under investigation. In aerobic systems, air is diffused from the bottom through the bed.

Andrews and Trapasso (1985) discuss several advantages that fluidized beds have over packed beds. Because gas bubbles can pass through the bed easily, smaller particles can be used. The use of smaller particles results in a larger biofilm surface area, which can handle higher organic loading. Also, the beds expand rather than clog as the biofilm grows. Growth can easily be controlled by removing particles from the top of the bed, washing them, and returning the cleaned particles to the reactor bottom.

Fluidized beds which use granular activated carbon as the solid material are referred to as biological activated-carbon systems. In these systems, adsorption and biodegradation of organics occurs simultaneously. This has advantages over a design in which the mechanisms occur in series. The granular activated carbon protects the system from organic shock loads, extends the retention time of the less readily biodegraded organics and adsorbs refractory compounds, just as it does in the powdered activated-carbon process. The microorganisms not only degrade the organics in the waste liquid, but also have been shown to regenerate the granular activated carbon (Goeddertz et al., 1988). A major drawback to the use of biological activated-carbon systems is the large capital investment in granular carbon required.

No information has been located on emissions of organic vapors from fluidized-bed reactors. For anaerobic systems, they are not assumed to be significant. For aerobic reactors, using diffused-air systems, air emissions are likely to be important.

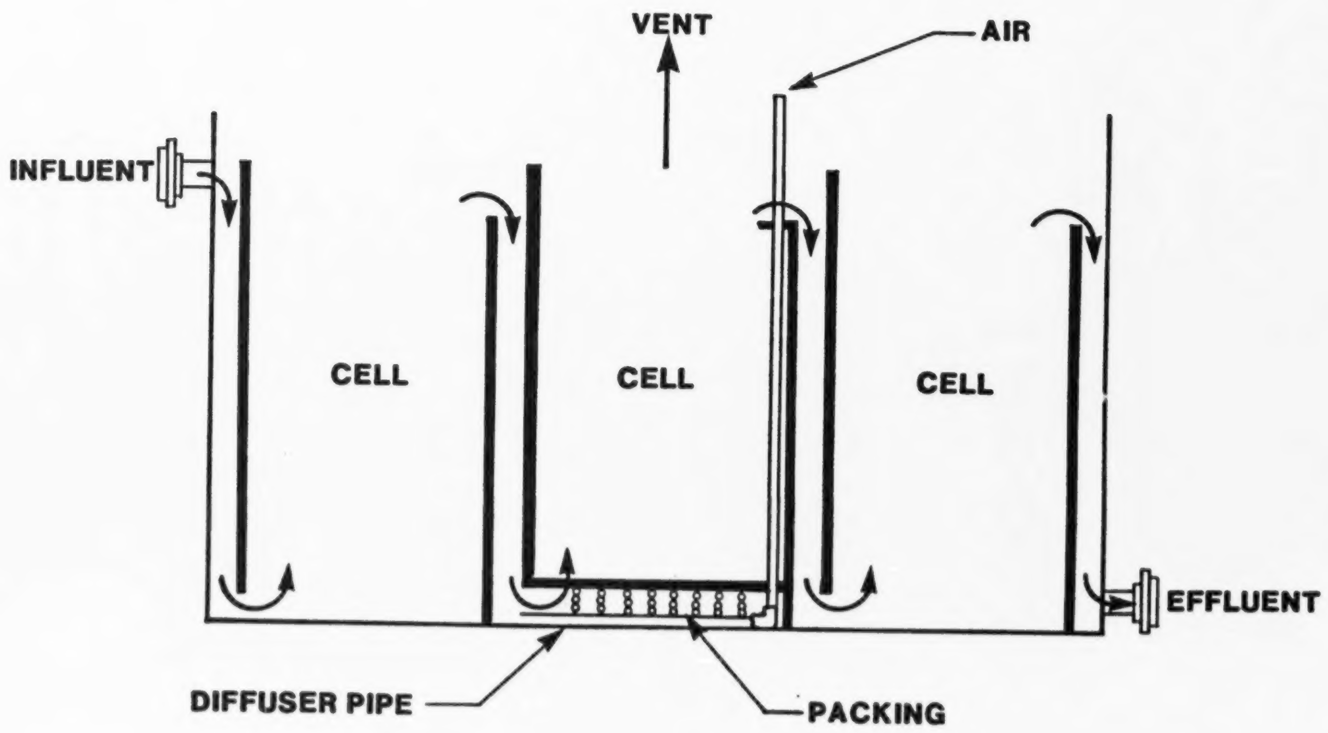
VENT
AIR
INFLUENT
CELL
CELL
CELL
EFFLUENT
DIFFUSER PIPE
PACKING

Figure 3.10. A submerged packed bed of compartmental design (from Chresand and Martinson, 1988).

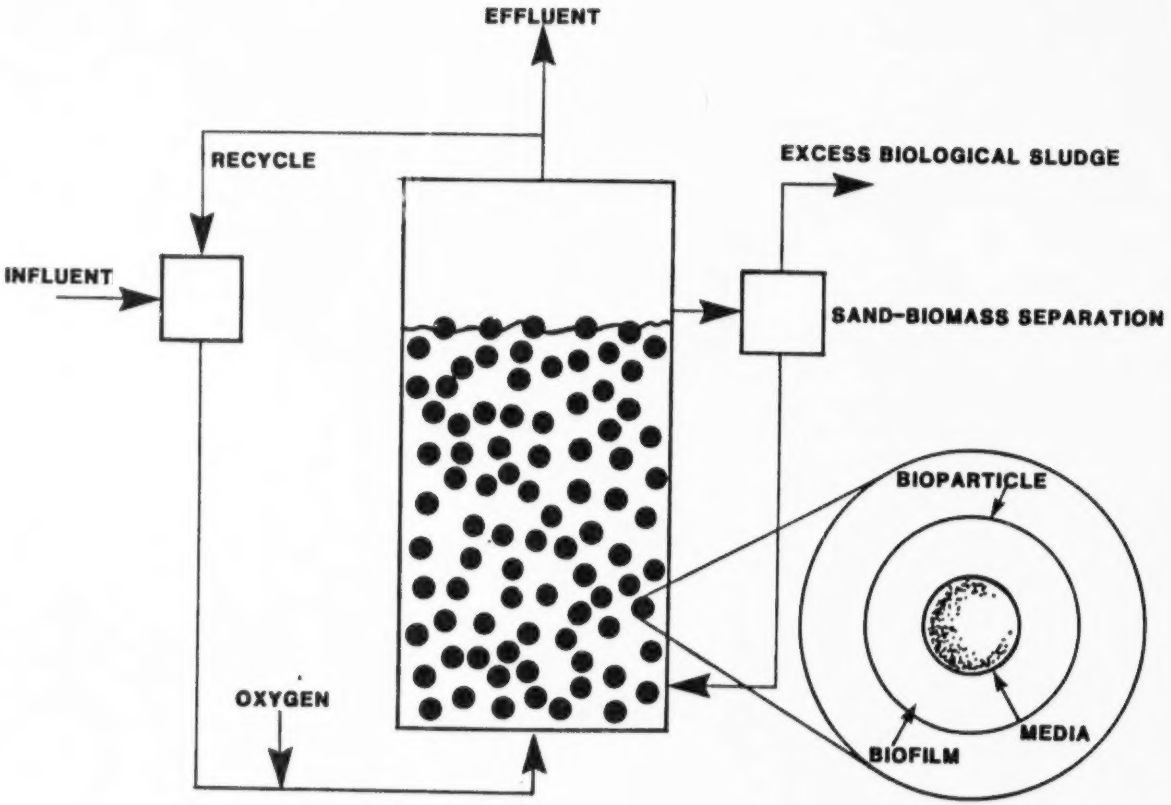
EFFLUENT
RECYCLE
EXCESS BIOLOGICAL SLUDGE
INFLUENT
SAND-BIOMASS SEPARATION
BIOPARTICLE
OXYGEN
MEDIA
BIOFILM

Figure 3.11. A fluidized-bed reactor (from Shieh et al., 1981).

3.4 SOIL INCORPORATION SYSTEMS

3.4.1 Land Treatment (Landfarming)

The spreading of organic wastes on agricultural land has been practiced for centuries. Farmers have relied on the mechanisms of aerobic microbial degradation, photolysis and other chemical reactions, adsorption, and volatilization to decompose the waste. Since the early 1950's, basically the same process has been used for the decomposition of some industrial and hazardous wastes, which can be in the form of liquid, sludge, or solid (e.g., contaminated soil). In 1982, more than 200 landfarming facilities handled hazardous waste (Hwang, 1982).

Four basic steps are involved in landfarming (Ross and Phung, 1980). First, the waste is applied to the soil by means of spray dispersal, surface application, or subsurface injection. The depth of injection is approximately 0.13 meters. Second, the waste is tilled into the upper soil layer, using farm equipment. The usual incorporation depth is approximately 0.15 to 0.3 meters. Tilling aerates the soil and thus, encourages growth of the naturally-occurring microorganisms. It also increases contact of the microorganisms with the waste. Third, the soil may be amended (e.g., nutrient addition) to encourage microbial growth. Finally, the soil is periodically remixed to keep it aerated.

The operation of wastewater land treatment systems is slightly different (Enfield et al., 1986). In rapid-infiltration systems, wastewater is applied to an infiltration basin at a rate greater than 5.3 m/yr. Either a constant head is maintained in the basin for a fixed amount of time or a specific volume of wastewater is applied. For both cases, the application of wastewater is followed by a drying cycle, when the soil is exposed to the air. In slow-rate systems, wastewater is used to irrigate a crop or a forest. The application rate depends on the soil and crop characteristics.

Ross and Phung (1980) report that only 3% of industrial sludge and 1% of industrial wastewater are suitable for land treatment. Wastes from the food, textile, wood and paper, leather-processing, and petroleum-refining industries are some that are amenable to treatment. It is currently the most attractive technique for treating oily sludge--about half of all refinery wastes are treated at landfarms (Thibodeaux and Hwang, 1982). A diverse group of organic compounds are associated with these sludges. The oil content by weight of the sludge can vary from 2 to 82 percent and water content can vary from 3 to 80 percent (Cadena et al., 1989). In addition to industrial wastes, pesticide-contaminated material and contaminated soil are successfully treated.

Landfarming facilities are designed to encourage the biological degradation of organic wastes incorporated into the upper soil layer. The soil and climatic characteristics of the site, the chemical characteristics of the waste and the operational techniques employed all influence the extent of biodegradation. Under normal conditions, biodegradation is considered to be the primary loss mechanism, followed by volatilization. Although photolysis and other chemical reaction occur at land treatment facilities, they are normally considered insignificant removal mechanisms. The factors affecting the land-treatment process are shown in Figure 3.12.

The emission of volatile organics and of contaminated dust both are potentially serious problems. Shen and Sewell (1988) estimate that 43,000 metric tons/year of 54 measured organic compounds (VOCs) are emitted from landfarming facilities in this country. The magnitude of emissions from a specific site depends on the application technique used, the frequency of tilling, the soil moisture content, the atmospheric conditions, and the properties of the waste and soil. Dust emissions, which increase as moisture content decreases and when the soil is retilled, can be controlled by keeping the soil surface moist. Water evaporation has been shown to increase volatile organic emissions by transporting soluble compounds to the soil surface.

Volatilization occurs during all stages of treatment, but is greatest during application and before tilling, unless subsurface injection techniques are used. Parker and Jenkins (1986) report that an average of 65 percent of six VOCs in an experimental wastewater were lost during spray application. These chemicals were chloroform, benzene, toluene, chlorobenzene, m-dichlorobenzene, pentane and hexane. Less than five percent removal was observed for PCB's, diethylphthalate, and phenanthrene. Subsurface injection minimizes losses due to volatilization.

Other potential environmental problems associated with landfarming are the possibility of surface runoff of contaminated water and of groundwater contamination. Neither problem is likely at a properly sited and operated facility.

The advantages of landfarming are its low cost and simplicity. Disadvantages include the need for large areas and long time periods. Also, the process is inhibited by high waste concentrations and by extreme weather conditions.

3.4.2 Composting

Composting is the controlled biological degradation of organic materials. Because the levels of moisture, oxygen, temperature and nutrients can be controlled, composting can achieve a higher degree of biological degradation of waste than achieved by landfarming, which often operates under sub-optimal conditions. While the composting of non-hazardous solid wastes has been practiced for many years, its application to hazardous waste treatment is new and still being researched. Insecticides in agricultural wastes have been composted successfully (Epstein and Alpert, 1980), as have soils contaminated with explosives and propellants (Williams and Ziegenfuss, 1988).

Composting is initiated by mixing the contaminated waste or soil with nutrients, if necessary, and with a bulking agent, such as wood chips or leaves. The bulking agent is important for maintaining the porosity of the mixture, thus allowing proper aeration. The inclusion of an inoculum, such as sludge, may also be needed. The mixture is then treated by one of several types of systems. Open systems are the most common. In open systems, the material is piled on platforms in long mounds, called windrows (Figure 3.13). Aeration is achieved by either mechanically turning the mixture periodically

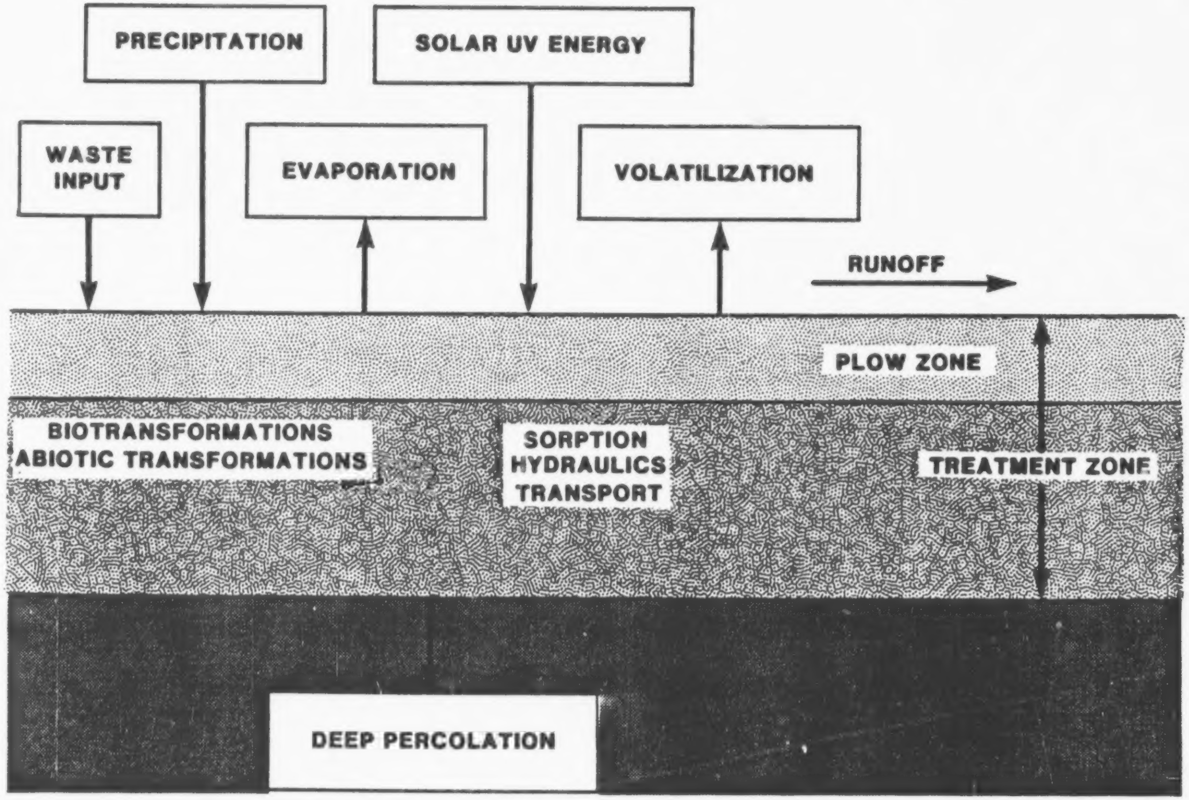
PRECIPITATION
SOLAR UV ENERGY
WASTE INPUT
EVAPORATION
VOLATILIZATION
RUNOFF
PLOW ZONE
BIOTRANSFORMATIONS
ABIOTIC TRANSFORMATIONS
SORPTION
HYDRAULICS
TRANSPORT
TREATMENT ZONE
DEEP PERCOLATION

Figure 3.12. The land-treatment process (from Short, 1986).

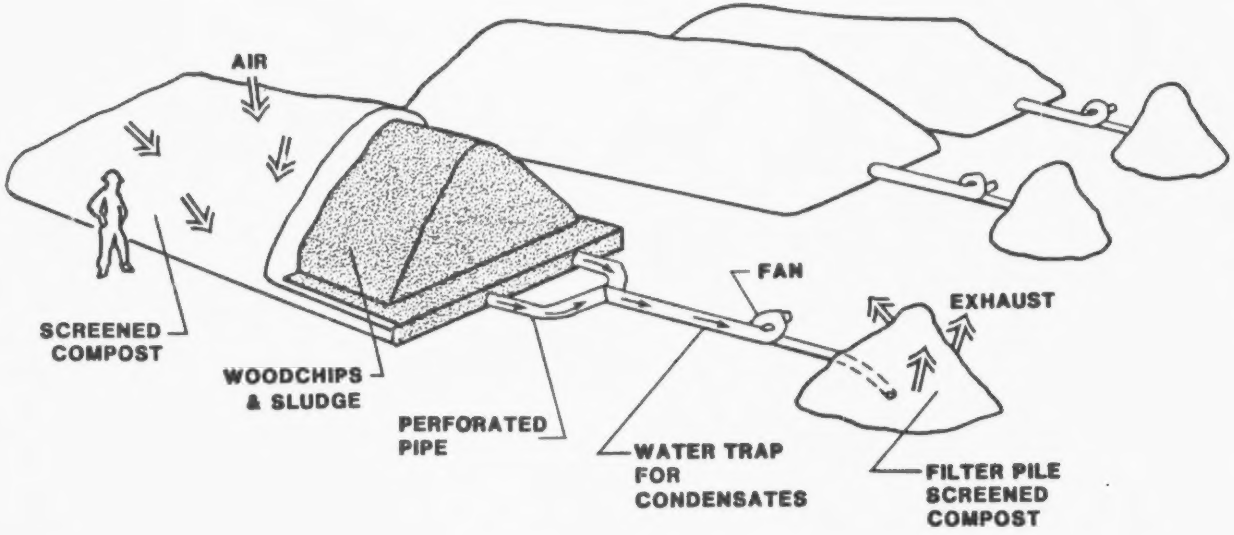
AIR
SCREENED COMPOST
WOODCHIPS & SLUDGE
PERFORATED PIPE
WATER TRAP FOR CONDENSATES
FAN
EXHAUST
FILTER PILE SCREENED COMPOST

Figure 3.13. Composting using forced aeration in an open system (from Epstein and Alpert, 1980).

or by forcing air through the static piles. Several closed systems are also in use (Hanstveit et al., 1988). In closed systems, the composting material is enclosed in vessels and continually mixed. Thus, the composting period is normally less than for open systems. Regulation of temperature and moisture content are both important in composting.

The magnitude of gaseous emissions from composting depends on the technique used. Turned windrow piles are likely to emit volatile organics on an order greater than landfarming, because of the higher temperatures involved. Forced aeration systems potentially produce an even higher degree of volatilization. Emissions from turned piles or from positive-pressure forced-air systems are harder to control than emissions from in-vessel systems or from forced-air systems using suction. For the latter two techniques, emissions are easily concentrated into a single air stream, which can be further treated. No data are currently available on emissions of volatile organics from composting facilities.

Composting has numerous advantages over landfarming. Because the process is controlled, the retention time and the land requirements are both much less than in landfarming. Water contamination problems are easily eliminated and air emissions can be collected and treated with proper design. On the other hand, composting is more capital- and labor-intensive than landfarming.

3.4.3 Soil Filter Beds (Biofilters)

Soil filter beds (Figure 3.14) rely on the mechanisms of adsorption, mechanical filtration, and aerobic biodegradation to treat air streams passing through the soil. The process has been used since the 1950's to control odors, such as from wastewater treatment plants or stock farms. Recently, particularly in Europe, they are being used to remove toxic vapors from industrial gas streams or from contaminant recovery systems used in environmental clean-up. The use of soil filter beds in the treatment of hazardous wastes is a new technology and limited data are available. Kosky and Neff (1988) report that soil filter beds can remove more than 90% of the hydrocarbons, such as toluene, butylacetate, and ethylacetate, in an air stream, given the proper moisture, nutrients, and pH conditions. Ryan et al. (1988) state that a soil biofilter is being planned for treatment of organic compounds being removed from contaminated groundwater. Other potential uses include the treatment of gases produced by air stripping or soil venting.

A typical soil filter bed has five major components (Kosky and Neff, 1988): 1) an air blower to push the waste air stream through the bed, 2) a system to distribute the air uniformly through the bed, 3) a system to maintain proper moisture content, which is crucial for removal efficiency, 4) a medium, either soil or peat compost, for microbial growth, and 5) an underdrain system to remove excess water. The soil bed is normally three to ten feet deep. Sewage sludge can also be incorporated into the soil or compost medium as an inoculum. Ottengraf and van den Oever (1983) state that maintaining a humidity of 50 to 70 percent is important for proper operation. They also note that the pH can drop with time in the bioreactor because of the production of acid intermediates by the microorganisms. Lime can be added to the beds to prevent a slowing of microbial activity with decreasing pH.

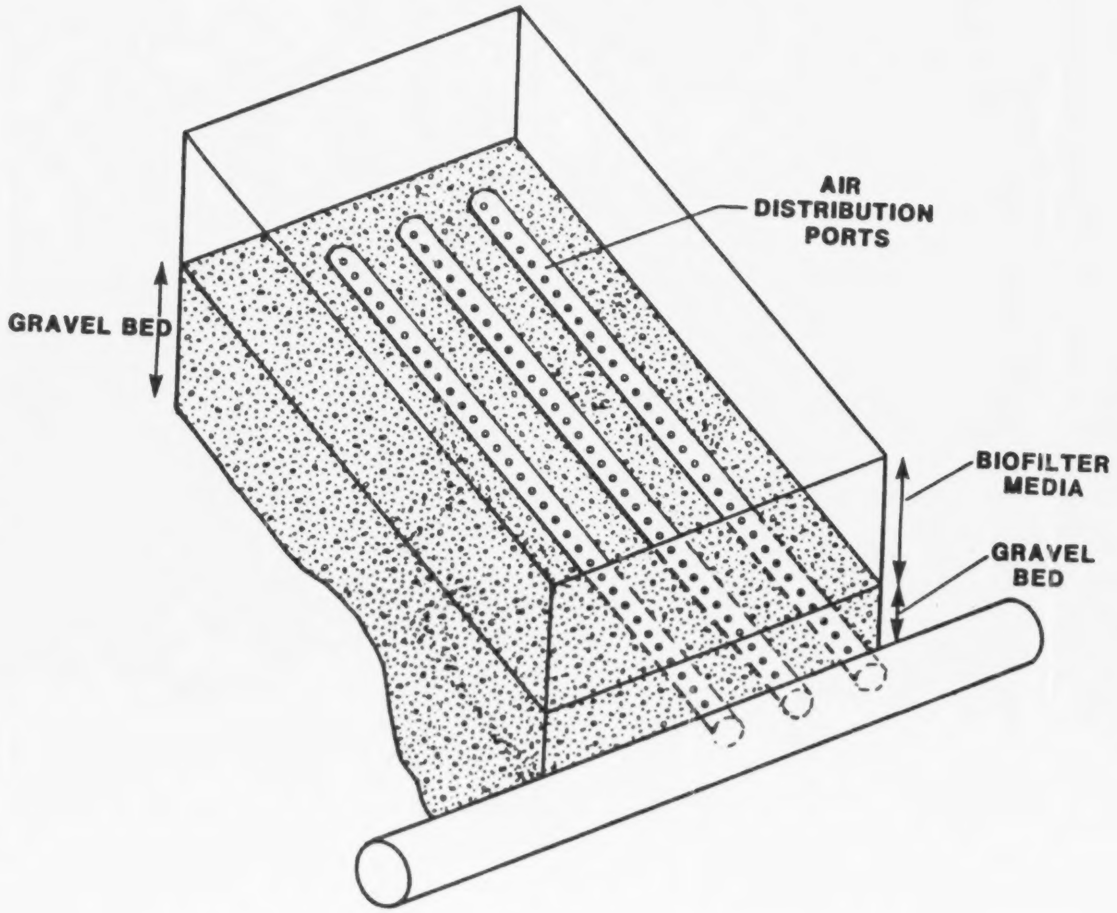
AIR
DISTRIBUTION
PORTS
GRAVEL BED
BIOFILTER
MEDIA
GRAVEL
BED

Figure 3.14. A typical soil-filter bed.

Since soil filter beds are already treating organics in the gaseous phase, volatilization is not a significant process. The magnitude of emissions from this process is directly related to the removal efficiency of the microorganisms and the adsorptive capacity of the medium. As more research is done on this process, its removal efficiency will be better defined. The design of the soil filter beds is such that the air exiting them could be captured for further treatment.

Work done thus far with soil filter beds indicates that they are simple to use, inexpensive, reliable and self-regenerating. They can be used intermittently. Microorganisms have been reported to survive two weeks between loadings (Ottengraf and van den Oever, 1983). In addition, the low cost and small space requirements of biofilters make them a promising bioremediation technology, particularly for use by small industries.

3.5 IN-SITU BIOREMEDIATION

The material on in-situ bioremediation presented here is based chiefly on the summaries of Lee et al. (1988) and PEI Associates (1988).

In-situ bioreclamation processes have potentially widespread application in the cleanup of contaminated subsurface materials, particularly sites contaminated with solvents and hydrocarbons. Both the saturated and the unsaturated zone can be treated, though more attention has been given to the saturated zone thus far. More than fifty aquifers have been remediated by in-situ methods. The porous mediums treated have been fractured dolomites, unconsolidated sands, and glacial tills.

For both the saturated and unsaturated zones, most in-situ work is based on the principle of enhancing the activity of indigenous microorganisms which degrade organics contaminating the subsurface. A number of methods are used to encourage microbial growth, including increasing the supply of oxygen and inorganics, increasing the temperature of the aquifer, and altering the pH of the environment. Emulsifiers can be added to facilitate the release of hydrophobic organics into the aqueous phase from which they are more readily degraded.

Pump and treat methods (Figure 3.15) are most commonly used for contaminated aquifers. Extraction and injection wells are installed. The flow of groundwater between the wells increases the degradation rate by increasing the available oxygen and nutrient supply. At the surface, the contaminated water can be treated by means of other processes and/or nutrients can be added before reinjection. This method, while being effective at cleaning an aquifer, is costly because of the equipment and energy required.

When treating immobile organics adsorbed to aquifer material, pump and treat methods are not as effective as the injection of nutrients and oxygen, which then are transported by natural gradients past the contaminated site.

A recent technology developed for aquifers contaminated with heavy metals is the permeable treatment bed. The technology relies on either biological or chemical reactions to remove pollutants. A permeable filter medium is placed

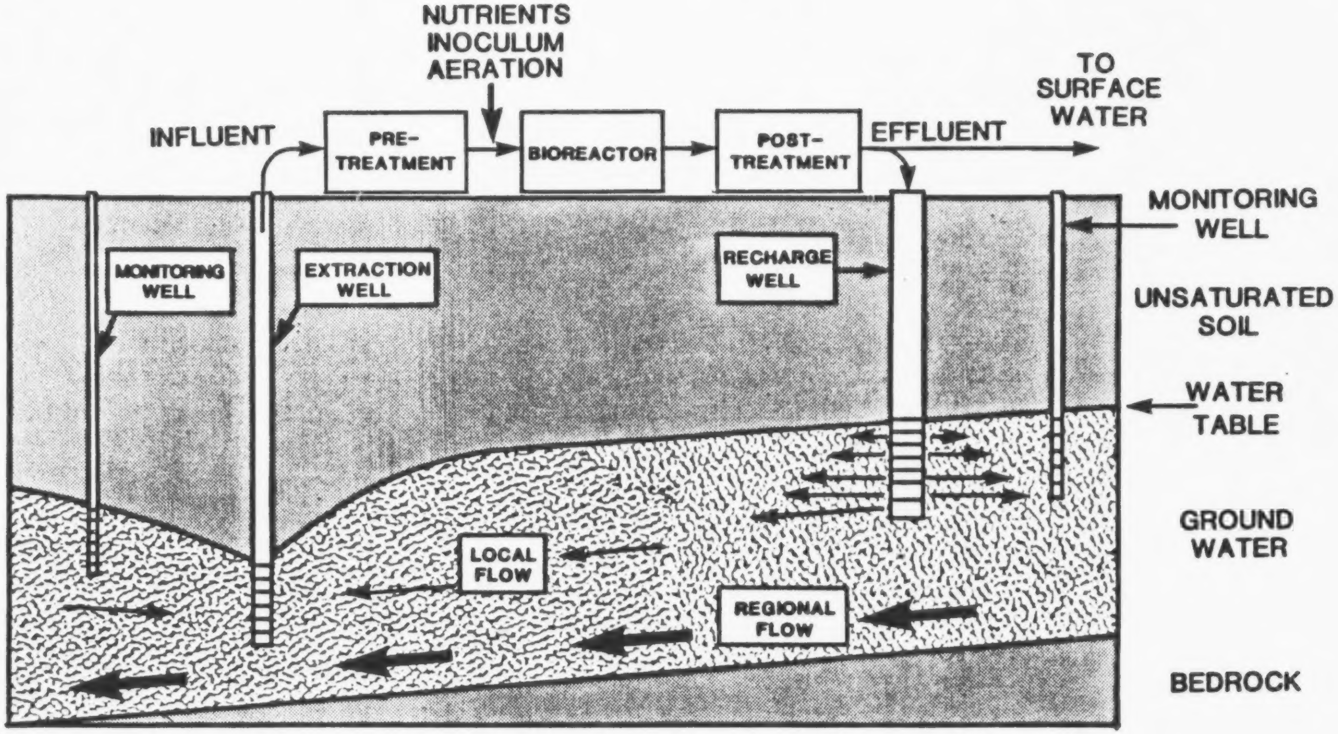
NUTRIENTS
INOCULUM
AERATION
INFLUENT
PRE-TREATMENT
BIOREACTOR
POST-TREATMENT
EFFLUENT
TO SURFACE WATER
MONITORING WELL
EXTRACTION WELL
RECHARGE WELL
MONITORING WELL
UNSATURATED SOIL
WATER TABLE
GROUND WATER
LOCAL FLOW
REGIONAL FLOW
BEDROCK

Figure 3.15. Pump-and-treat bioremediation of a contaminated aquifer (from PEI Associates Inc., 1988).

in the saturated zone downgradient from a contaminant plume. For chemical treatment beds, the filter medium is usually crushed limestone or glauconitic greensands, which adsorb the metals. In the case of bioremediation, microorganisms growing in the barrier degrade the organics in the plume and precipitate the heavy metals. A permeable treatment bed must be placed with care so that the plume does not pass around it. Another potential problem is clogging of the permeable bed. The permeable bed must be removed after treatment to prevent remobilization of the metals. Because this is a new technology, little information is available about it.

Altering the soil environment to enhance microbial growth is the most common way to treat the unsaturated zone. Air sparging or the addition of hydrogen peroxide can supply oxygen and usually nutrients are added. An additional important factor for in-situ bioremediation of the unsaturated zone is soil moisture content. A high moisture content hinders oxygen transport and low moisture content hinders microbial activity.

In-situ landfarming methods can be used to treat shallow (i.e., less than 50 centimeters) soil contamination problems without expensive excavation (Hanstveit et al., 1988). The affected area is cleared of surface debris and the soil is tilled to supply oxygen. If necessary, fertilizers can be added and pH can be controlled by liming the site. Ryan et al. (1988) describe the effective treatment of polyaromatic hydrocarbons at an abandoned wood preserving facility. Removals of 90% after 193 days were achieved.

Partitioning of a volatile organic can occur at the interface of the saturated and unsaturated zones in the subsurface. Thus, it is possible for a dissolved organic in a polluted aquifer to contaminate the unsaturated zone above. In the unsaturated zone, the volatile organic can move upward by gas-phase diffusion, eventually reaching the soil surface, where it volatilizes. Swallow and Gschwend (1983) present both laboratory and field evidence that air emissions of volatile organics from polluted aquifers can occur. However, because emissions from saturated in-situ remediation sites must pass through the unsaturated zone, estimates of air emissions can be made by modeling the unsaturated zone and supplying a source term at the saturated/unsaturated boundary. In general, emissions from contaminated aquifers are expected to be relatively insignificant. Bomberger et al. (1983) state that diffusion to the surface is slow at depths of 25 cm. Most water tables are located at depths on the order of meters. For soils contaminated with volatile organics in the unsaturated zone, however, the processes of gaseous diffusion and volatilization can not be ignored, particularly if air is being sparged into the soil. Data have not been located that indicate the magnitude of emissions from in-situ remediation sites.

3.6 PHYSICAL REMEDIATION PROCESSES

Two physical remediation processes, which can be used in conjunction with bioremediation processes, are discussed in this section. They are included because there is a high potential for air emission of organics associated with them.

3.6.1 Soil Venting

Soil venting or vapor extraction is a relatively new in-situ technology, which uses physical processes to remediate soil contaminated by volatile and semi-volatile organics. It is described by Massmann (1989). A vacuum applied to the soil induces advective transport of contaminant vapors, thus removing volatile pollutants from the soil. As they are extracted, more organics in the liquid phase volatilize. A typical system consists of a vacuum pump connected to a series of wells completed in the unsaturated zone. Air injection wells can also be used in conjunction with the extraction wells to control flow (Figure 3.16). The extraction rate is low, typically 30-300 cubic ft./min. per well. Depending on the type of vapors extracted, further treatment of the gas stream may be needed before it is released to the atmosphere.

The effectiveness of soil venting depends on a number of site-specific factors, including the soil permeability, clay content, and moisture content, and the contaminant's characteristics. The types of contaminants which can be treated by soil venting are pure volatile chemicals, such as trichloroethylene, and mixtures, such as gasoline and other petroleum products. The response of petroleum products to treatment is difficult to predict, because the individual components of the waste have a wide range of properties.

Success depends on establishing an air-flow field which intersects the contaminated soil and sufficiently rapid mass transfer rates (Baehr, in press).

Initial testing and research indicates that soil venting is effective, economical, and more rapid than other types of in-situ remediation. While soil venting is a physical process, it is an effective aid to in-situ bioremediation. By setting up a flow of air in the unsaturated zone, it stimulates the growth of microorganisms.

3.6.2 Soil Washing

Valine et al. (1989) describe a process, known as soil washing. Soil washing is an accepted means of treating contaminated soil in Europe, but a relatively new technology in this country. The contaminated soil is first rough-screened to remove large debris. Next, it is mixed with water and the resulting slurry is treated in a series of intensive scrubbing and physical separation steps. The scrubbing frees the highly contaminated fine soil particles (the clays, silts, and humus) from the larger sands and gravels. It also cleans the surfaces of the larger particles by means of abrasion. The contaminated fine particles and water can then be treated biologically (e.g., activated sludge) or by some other means (e.g., incineration). The chief advantage of this method is that it results in significant volume reduction of contaminated soil. Valine et al. (1989) reduced the volume of soil needing biological treatment by approximately 75% when they used soil washing at a contaminated wood-preserving plant.

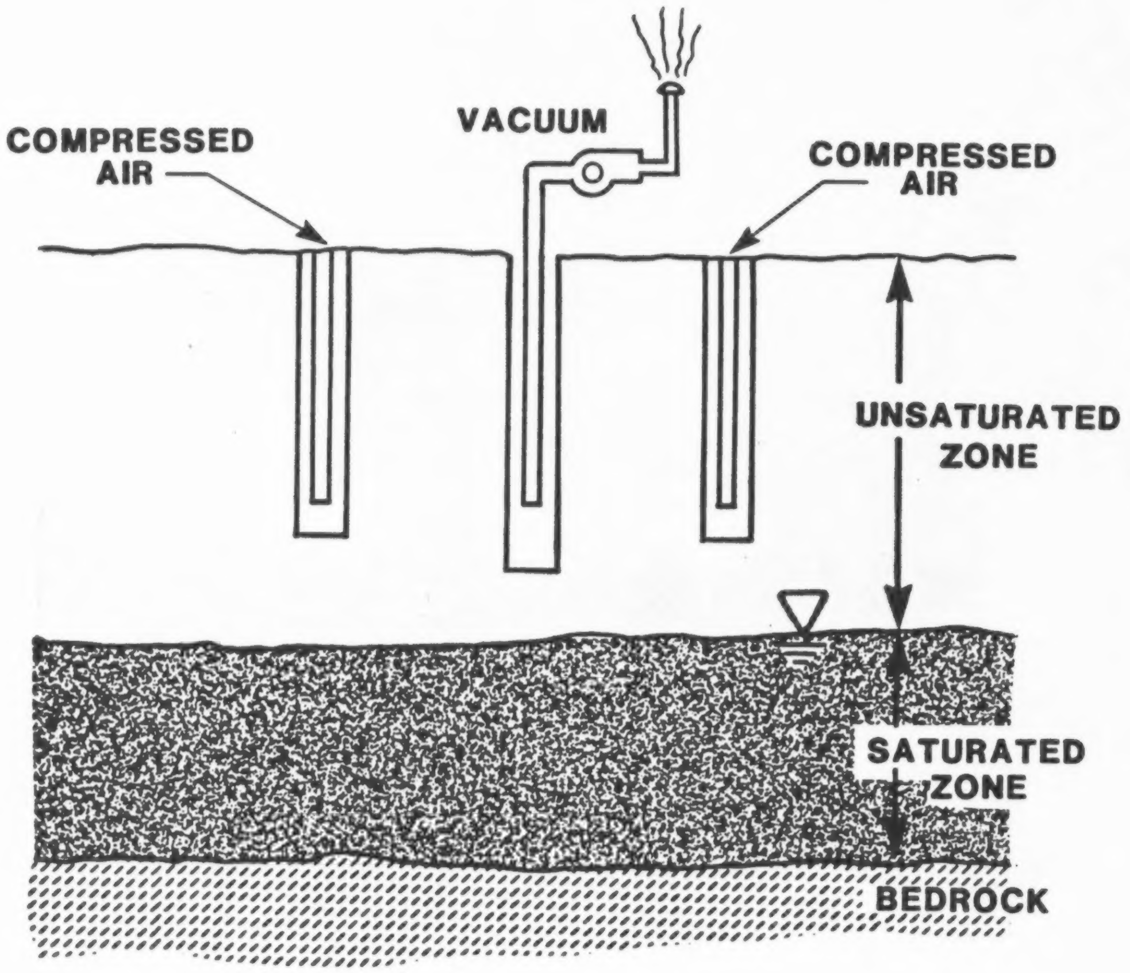
COMPRESSED AIR
VACUUM
COMPRESSED AIR
UNSATURATED ZONE
SATURATED ZONE
BEDROCK

Figure 3.16. The soil-venting process (adapted from Baehr and Hoag, 1988).

Because of the agitation and mixing involved, soil-washing facilities exposed to the air could be a significant source of air emissions of volatile organics. No data are available on the magnitude of those emissions.

SECTION 4

MODELS OF SUSPENDED-GROWTH SYSTEMS

This section summarizes the current status of models which can be used to estimate the fate of organic pollutants during treatment in four different suspended-growth systems: activated-sludge, powdered activated carbon treatment, sequencing batch reactors, and surface impoundments.

4.1 ACTIVATED-SLUDGE MODELS

4.1.1 Introduction

Most research on the fate of toxic organic pollutants in wastewater has focused on aeration of activated-sludge treatment facilities. The research has shown that one or more of four removal mechanisms are important, depending on the characteristics of the chemical and the operating conditions of the facility. The four mechanisms are biodegradation, passive volatilization, stripping and adsorption. If a pollutant is not removed from the wastewater by one of these mechanisms, it will be discharged with the effluent. A number of models have been developed over the last ten years to simulate the fate of specific toxic compounds in the aeration tank of an activated-sludge facility. Other components of the activated-sludge facility (e.g., the clarifier) have not been modeled. It is expected that emissions of pollutants for these other components will be slight relative to emissions from the aeration tank. If desired, a settling tank or clarifier can be modeled using equations presented in Section 4.4.2 for quiescent impoundments. The biodegradation term should be set to zero.

Activated-sludge units can experience shock loading of toxic chemicals, which slows or stops biological activity. In addition, the biomass in the aeration tank may not be able to degrade toxic organics which enter the tank at infrequent intervals, because the biomass is not acclimated to the waste. To model air emissions under such circumstances, any of the models described in this section can be used by setting the biodegradation rate constant to zero.

Excluding biological activity from the modeling process provides a conservative estimate of emissions under normal operating conditions. Because data and experience in modeling the kinetics of biodegradation are both limited, it is recommended that this conservative estimate be included as part of a screening study.

Aeration is achieved either by subsurface sparging with diffused air bubbles or by mechanical agitation. Diffused-air systems can be simulated by means of mathematical models developed by Namkung and Rittmann (1987), Blackburn et al.

(1985), or the U.S. EPA (1987b). Hwang (1981) and the U.S. EPA (1987b) provide mathematical models for mechanically-aerated systems. A computer model, called NOCEPM, developed by Barton (1987) for the National Council of the Paper Industry for Air and Stream Improvement (NCASI), can simulate both types of aeration. Models for both types of aeration are also included in a computer spreadsheet, called CHEMDAT6, developed by the U.S. EPA (1987b). These models are described in detail in Sections 4.1.2 through 4.1.6. Their characteristics and input requirements are summarized in Tables 4-1 and 4-2. In Section 4.1.7 additional models are briefly summarized.

All the models of the activated-sludge process have common characteristics. The models assume that the tank is completely mixed, that the effluent concentration is not known, and that no non-aqueous liquids are present. In addition, they all assume steady-state conditions exist. Given that the concentration of specific compounds in influent wastewater can vary over several orders-of-magnitude during a day, this limits the accuracy of the models. In general, steady-state models of suspended-growth systems are best used for screening purposes (e.g., to determine the likely fate of a specific chemical). Other common assumptions are that the two-film theory adequately represents mass transfer to the air and that the concentration of the volatile organic in the air above the tank is zero.

The models differ mainly in two areas: the determination of passive volatilization and/or stripping rates, and the determination of biodegradation rates.

Namkung and Rittmann (1987) and U.S. EPA (1987b), assume the air bubbles in the subsurface are saturated with the compound of interest. By assuming equilibrium conditions, calculations are simplified because a mass transfer coefficient is not needed. This assumption may or may not be valid, depending on the chemical. Blackburn et al. (1985) use a first-order stripping rate equation, developed by fitting a power function to data. Research by the authors indicates that the equation is accurate in pure water for compounds with dimensionless Henry's law constants ranging over four orders-of-magnitude (1×10^{-1} to 1×10^{-5}). The stripping rate equation included in the NCASI model (Barton, 1987) allows partial saturation of the air bubbles and thus is conceptually the most accurate. Because stripping is a more significant source of air emissions than passive volatilization, the Namkung-Rittmann model (1987) and the Blackburn et al. model (1983) neglect terms for volatilization.

The effects of mechanical aeration are incorporated into the Hwang (1981) and U.S. EPA (1987b) models by including two different mass transfer coefficients: one for the turbulent surface area and one for the convective surface area. Only the NCASI model distinguishes between stripping from spray droplets caused by mechanical aeration and volatilization from the surface of the tank.

Most of the activated-sludge models assume pseudo-first-order biodegradation kinetics. The rate of biodegradation is dependent on both the concentration of the toxic organic and the concentration of the biomass. However, because the biomass concentration is assumed constant and is an input parameter, the equation becomes first-order for the toxic organic chemical. Hwang (1981)

TABLE 4-1. SUMMARY MATRIX OF ACTIVATED SLUDGE MODEL CHARACTERISTICS

Characteristics	Model						
	Blackburn et al.	EPA[1] & CHEMDAT6[1]	EPA[2] & CHEMDAT6[2]	Hwang[3]	Hwang[4]	Namkung & Rittmann	NOCEPM
Aeration Method							
Surface aeration		X		X	X		X
Diffused aeration	X		X			X	X
Time Domain							
Steady-state	X	X	X	X	X	X	X
Dynamic							
Spatial Domain							
1-dimensional	X	X	X	X	X	X	X
Flow							
Completely-mixed	X	X	X	X	X	X	X
Plug							
Degradation/ Transformation							
Volatilization		X	X	X	X		X
Stripping	X		X			X	X
Biodegradation	X	X	X	X	X	X	X
Sorption	X			X		X	X
Solution Technique							
Analytical							
--hand calculation	X	X	X	X	X	X	
--computer		X	X				X
Numerical							
Availability							
Published paper/report	X	X	X	X	X	X	X
Proprietary							X
Public domain		X	X				

1 - Mechanically aerated system
2 - Diffused air system
3 - With adsorption
4 - Without adsorption

TABLE 4-2. SUMMARY MATRIX OF ACTIVATED SLUDGE MODEL INPUT DATA

	Model								
Data Required	Blackburn et al.	CHEMDAT6[1]	CHEMDAT6[2]	EPA[1]	EPA[2]	Hwang[3]	Hwang[4]	Namkung & Rittmann	NOCEPM
Tank Characteristics									
Volume	X			X	X			X	X
Total surface area		X	X	X	X	X	X		X
Turbulent surface area		X		X	X	X	X		
Quiescent surface area				X	X	X	X		
Depth		X	X						
Flow Rates									
Wasted sludge						X			
Sparged gas	X		X		X			X	X
Total (fresh+recycle)	X	X	X	X	X			X	X
Fresh-feed						X	X		
Recycled						X	X		
Concentration									
Compound influent	X	X	X	X	X	X	X	X	X
Wasted cells								X	X
Active cells		X	X	X	X	X	X	X	X
Maximum adsorbed						X			
Total substrate minus compound considered						X			
TOC influent	X	X	X	X	X				
Effluent total suspended solids									X

1 - Mechanically aerated system
2 - Diffused air system
3 - With adsorption
4 - Without adsorption

(continued)

TABLE 4-2. SUMMARY MATRIX OF ACTIVATED SLUDGE MODEL INPUT DATA (continued)

Data Required	Model								
	Blackburn et al.	CHEMDAT6[1]	CHEMDAT6[2]	EPA[1]	EPA[2]	Hwang[3]	Hwang[4]	Namkung& Rittmann	NOCEPM
Coefficients/ Constants									
Henry's Law	X			X			X		X
Octanol/water partition	X						X		X
Temperature		X	X		X			X	X
Volatilization constant:									
--turbulent area				X	X	X	X		
--quiescent area				X	X	X	X		
Adsorption constant:									
--compound						X			
--total subtrate						X			
Growth yield coefficient for TOC	X								
Microorganism decay coefficient for TOC	X								
Biodegradation constant:									
--compound	X			X	X	X	X	X	X
--TOC	X	X	X						
Lipid density	X								
Lipid weight fraction	X								
Molecular weight									
--compound									X
Surface reaeration rate									X
Diffusivity in water									
--compound									X

1 - Mechanically aerated system
2 - Diffused air system
3 - With adsorption
4 - Without adsorption

(continued)

TABLE 4-2. SUMMARY MATRIX OF ACTIVATED SLUDGE MODEL INPUT DATA (concluded)

Data Required	Model Blackburn et al.	CHEMDAT6^1	CHEMDAT6^2	EPA^1	EPA^2	Hwang^3	Hwang^4	Namkung& Rittmann	NOCEPM
Other									
Hydraulic residence time						X	X		
Mean cell residence time	X								
Number of compounds in multicomponent substrate				X	X				
Total horsepower		X							X
Oxygen transfer efficiency		X							X
Wind velocity		X	X						X
Number of impellers		X							
Impeller diameter		X							
Impeller speed		X							
Power transfer efficiency		X							

1 - Mechanically aerated system
2 - Diffused air system
3 - With adsorption
4 - Without adsorption

incorporates Grau kinetics into his model. For Grau kinetics, the biodegradation rate is dependent on biomass concentration and the substrate concentration divided by the initial substrate concentration. A similar kinetic relationship is used in the U.S. EPA (1987b) models. All of the models assume that the entire active biomass degrades each compound. While this is probably not true, no methods are available at the present time to determine the fraction of the biomass degrading a particular compound, and thus, it is a necessary assumption.

The activated-sludge process has been modeled more than most bioremedial processes. The current models are appropriate for screening purposes, but need to be more extensively field tested before they can be used with confidence to estimate emissions at specific sites.

4.1.2 The Namkung-Rittmann Model

4.1.2.1 Summary--

Namkung and Rittmann (1987) present a simple mathematical model of the fate of volatile organics in the aeration tank of an activated-sludge treatment system. The tank is sparged with diffused air bubbles. The removal mechanisms included in the steady-state mass-balance model are stripping, adsorption, and biodegradation. The important equations in the model are listed in Table 4-3. The major assumptions associated with these equations, along with comments about the effects of some of the assumptions, are listed below.

The assumptions made in developing the overall mass balance equation (Equation 1 in Table 4-3) include:

1) The liquid outflow, which is the sum of the wasted sludge flow and the effluent flow, equals the inflow.

2) Adsorption, biodegradation, stripping, and removal with the effluent are the only significant removal mechanisms.

3) The removal mechanisms (sorption, biodegradation, and stripping) are independent of each other and thus the total amount of contaminant removed is the sum of the amounts removed by each process. In reality, these processes are interdependent. Govind and Wang (1989) maintain that sorption reaches equilibrium more rapidly than stripping or biodegradation. Thus, they believe this and other fate models should be modified so that biodegradation and stripping rates are dependent on liquid concentrations which have been corrected for sorption first.

4) Even though flow in conventional municipal aeration tanks is often best described as plug flow, the aeration tank is modeled as a completely-mixed reactor. Assuming a completely-mixed system results in lower average solute concentrations than may actually occur and thus, may underestimate emissions. This assumption is made, though, in order to simplify the mathematics of the model.

TABLE 4-3. IMPORTANT EQUATIONS IN THE NAMKUNG/RITTMANN MODEL

1) General steady-state mass balance

$$0 = Q(S^o - S) + R_{bio} + R_{ads} + R_{vol} \tag{1}$$

where

Q = wastewater flow rate to the aeration tank (m^3/day)

S_o = individual compound concentration in influent (g/m^3)

S = concentration of individual compound in aeration tank (g/m^3)

R_{bio} = compound biodegradation rate (g/day)

R_{ads} = compound adsorption rate (g/day)

R_{vol} = compound stripping rate (g/day)

2) Stripping reaction rate

$$R_{vol} = -\frac{GHS}{RT} \tag{2}$$

where

G = gas volumetric flow rate (m^3/day)

H = Henry's Law constant (atm-m^3/mole)

R = universal gas constant ($=8.206 * 10^{-5}$ m^3-atm/^{o}K-mole)

T = absolute temperature (^{o}K)

3) Adsorption reaction rate

$$R_{ads} = -(3.345 * 10^{-7})Q^w X_v^w K_{ow} \tag{3}$$

where

Q^w = wasted sludge flow rate (m^3/day)

X_v^w = wasted cells concentration (g VSS/m^3)

K_{ow} = octanol/water partition coefficient (m^3 H_2O/m^3 octanol)

TABLE 4-3. IMPORTANT EQUATIONS IN THE NAMKUNG/RITTMANN MODEL (concluded)

4) Biodegradation reaction rate

$$R_{bio} = -k_1 X_a S V \qquad (4)$$

where

V = volume of aeration tank (m^3)

X_a = active cell concentration (g VSS/m^3)

k_1 = apparent first-order biological reaction constant (m^3/g VSS day)

5) Steady-state reactor concentration

$$S = \frac{QS^o}{Q + \frac{GH}{RT} + (3.345 * 10^{-7}) Q^w X_v{}^w K_{ow} + K_1 X_a V} \qquad (5)$$

5) Volatilization, adsorption, and biodegradation from the settling tanks and other parts of the treatment facility are not significant (i.e., only the aeration tank is modeled). This assumption will lead to some underestimation of emissions, but is a commonly made assumption by researchers.

6) Steady-state conditions exist.

7) The influent substrate concentration is soluble and its concentration is constant. In reality, the concentration of a particular compound in the aeration tank can vary widely during a short period of time.

Assumptions related to the development of the stripping rate equation (Equation 2 in Table 4-3) are:

1) Negligible quantities of the modeled compound are in the inlet gas.

2) When the gas bubbles exit the liquid, their partial pressure is in equilibrium with the solute concentration.

3) Volatilization across the air/water interface at the surface of the reactor is not modeled. While stripping is a more significant source of air emissions, because the gas/liquid interfacial area involved is much greater, the exclusion of volatilization from the model will underestimate emissions to some extent (Corsi et al., 1989).

4) No correction factor for kinetic limitations is considered (i.e., transfer through the liquid/gas interface is not limiting). Pincince (1988) explains that for some volatiles, this assumption is valid. For volatiles with high Henry's law constants and low mass transfer coefficients, stripping will be overestimated.

Assumptions related to the development of the adsorption rate equation (Equation 3 in Table 4-3) are:

1) A linear adsorption isotherm is valid.

2) Because the solids consist chiefly of biological cells, the mass fraction of organic carbon in the solids, f_{oc}, equals 0.531. This is based on a formula for cell composition of $C_5H_7O_2N$.

Assumptions related to the development of the biodegradation rate equation (Equation 4 in Table 4-3) are:

1) No microbial solids are in the influent flow.

2) Monod kinetics can be simplified to a first-order relationship. This is a reasonable assumption as long as the compound is present in low concentrations in the tank.

3) The oxygen supply does not limit microbial activity.

4) Trace organics are biodegraded by a secondary utilization mechanism (i.e., biological growth and maintenance is provided by another substrate, such as biological oxygen demand (BOD)). As a result:

   a) Active cell concentration, X_a, can be approximated as the total active cell mass in the reactor.

   b) The first-order biodegradation constant, k_1, can be set equal to 0.1 m^3/g VSS/day for biodegradable compounds and 0.0 m^3/g VSS/day for non-biodegradable compounds. The authors show that increasing the value of k_1, if k_1 is greater than 0.1 m^3/g VSS/day, does not affect the removal of volatile organics by means of secondary utilization.

4.1.2.2 Input Requirements--

The input parameters which need to be specified by the user are listed below. Appropriate units are shown in Table 4-3.

1) The volume of the aeration tank (V)

2) The wastewater flow rate to the aeration tank (Q)

3) The wasted sludge flow rate (Q^w)

4) The gas volumetric flow rate (G)

5) The individual compound concentration in the influent (S_o)

6) The concentration of wasted cells (X_v^w)

7) Henry's Law constant (H)

8) Octanol/water partition coefficient (K_{ow})

9) The first-order biological reaction constant (k_1)

10) The active cell concentration (X_a)

11) Absolute temperature (T)

Many of these parameters are easily determined from the literature or are readily known characteristics of the facility being modeled. The authors recommend a value for the biological reaction constant, k_1, which is normally hard to approximate. The individual compound concentration in the influent, S_o, will normally not be known and will need to be measured.

4.1.2.3 Output Description--

In the model, Equation 5 in Table 4-3 is first solved to obtain the concentration of the individual compound in the aeration tank. Once this steady-state value is known, the fate of the organic can be determined by solving Equations 2 through 4 for the rates of stripping, adsorption, and biodegradation respectively.

4.1.2.4 Resource Requirements--

Once the values of the input parameters have been specified, this model can easily be solved using a calculator. The equations could also be easily programmed for use on a computer if the model were to be used repetitively.

4.1.2.5 Ease of Use--

The model is very straight-forward and relies on input data which can be obtained or estimated without extensive experimentation or laboratory work. It is therefore an easy model to apply.

4.1.2.6 Previous Applications--

The authors applied the model to data collected at two publicly-owned treatment facilities and found good agreement between the model predictions and the field data (Namkung and Rittmann, 1987). They also found that their results are consistent with the lab-scale experimental results of three other authors (Namkung and Rittmann, 1987).

4.1.2.7 Availability/Documentation--

The model is described in Namkung and Rittmann (1987).

4.1.3. The Blackburn et al. Model

4.1.3.1 Summary--

Blackburn et al. (1985) and Blackburn (1987) develop a steady-state mathematical model of a continuous-flow, completely-mixed activated sludge aeration tank. The tank is aerated by means of coarse-bubble diffusion. The model couples equations describing microbial growth in terms of available total organic carbon (TOC) with equations describing the fate of a specific compound in the tank. Loss of the specific compound occurs through biodegradation, sorption, stripping, and effluent flow. The important equations in the Blackburn et al. model are listed in Table 4-4. The equations and the major assumptions associated with them are discussed below.

The general material balance is shown in Equation 3 of Table 4-4. The assumptions made in developing this material balance include:

1) The aeration tank is a completely-mixed reactor.

2) Steady-state conditions exist.

TABLE 4-4. IMPORTANT EQUATIONS IN THE BLACKBURN et al. MODEL

For Total Organic Carbon (TOC)

1) Effluent TOC concentration

$$T_{ae} = \frac{1/\theta_c + k_d}{Y\ K^1} \tag{1}$$

2) Biological solids concentration

$$X = \frac{Y\ Q_a(T_{ao} - T_{ae})}{V\ (1/\theta_c + k_d)} \tag{2}$$

where

X = concentration of biological solids in the reactor (mg/L of MLSS)

K^1 = substrate utilization rate constant (L/mg-day)

Q_a = influent flow (L/day)

T_{ao} = influent TOC (mg/L)

T_{ae} = effluent TOC (mg/L)

V = reactor volume (L)

k_d = microorganism decay coefficient (1/day)

θ_c = mean cell residence time (days)

Y = growth yield coefficient (mg MLSS/mg TOC)

For a specific compound

3) General mass balance

$$-V\left(\frac{dC_{ae}^{tot}}{dt}\right) = Q_a\ C_{ao} - (Q_a - Q_w)\ C_{ae} - Q_w\ C_{ae} - V\left(\frac{dC_{ae}^{sp}}{dt}\right) - V\left(\frac{dC_{ae}^{b}}{dt}\right) - V\left(\frac{dC_{ae}^{st}}{dt}\right) \tag{3}$$

where

V = aeration basin volume (L)

$\frac{dC_{ae}^{tot}}{dt}$ = total net rate of change of substrate soluble concentration in the reactor (mg/L-day) (equal to 0 at steady-state)

TABLE 4-4. IMPORTANT EQUATIONS IN THE BLACKBURN et al. MODEL (continued)

Q_a = influent flow (L/day)

Q_w = waste sludge flow (L/day)

C_{ao} = soluble concentration of substrate in the influent (mg/L)

C_{ae} = soluble concentration of substrate in the effluent (mg/L)

$\frac{dC_{ae}^{sp}}{dt}$ = net rate of change in soluble concentration of substrate in the reactor due to sorption to biological solids (mg/L-day)

$\frac{dC_{ae}^{b}}{dt}$ = net rate of change in soluble concentration of substrate in the reactor due to bio-oxidation (mg/L-day)

$\frac{dC_{ae}^{st}}{dt}$ = net rate of change in soluble concentration of substrate in the reactor due to stripping (mg/L-day)

4) Stripping rate

$$\frac{dC_{ae}^{st}}{dt} = \frac{Q_{air}}{V} \; 6.18 * 10^{-5} \; {H_c}^{1.045} \; C_{ae} \tag{4}$$

where

Q_{air} = air flow (L/day)

H_c = Henry's Law constant (torr-L/g-mol)

5) Sorption rate

$$\frac{dC_{ae}^{sp}}{dt} = \frac{X \; V \; K_{ow} \; f_L \; C_{ae}}{1000 \; \rho_L \; \theta_c} \tag{5}$$

where

K_{ow} = octanol-water partition coefficient (concentration ratio)

f_L = lipid weight fraction of biological solids (μg lipid/μg dry solids)

ρ_L = density of lipids (g/L)

θ_c = mean cell residence time (days)

TABLE 4-4. IMPORTANT EQUATIONS IN THE BLACKBURN et al. MODEL (concluded)

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6) Biodegradation rate

$$\frac{dC_{ae}^{b}}{dt} = K^{1} X C_{ae} \tag{6}$$

7) Steady-state reactor concentration

$$C_{ae} = \frac{Q_a C_{ao}}{Q_a + \frac{X V K_{ow} f_L}{1000 \rho_L \theta_c} + V \frac{Q_{air}}{V} 6.18 * 10^{-5} H_c^{1.045} + V K^{1} X} \tag{7}$$

8) Percent removal of substrate by each mechanism

$$REM_{sp} = \frac{A}{1 + A + S + B} * 100 \tag{8}$$

$$REM_{st} = \frac{S}{1 + A + S + B} * 100 \tag{9}$$

$$REM_{b} = \frac{B}{1 + A + S + B} * 100 \tag{10}$$

$$REM_{e} = \frac{1}{1 + A + S + B} * 100 \tag{11}$$

where

$$A = \frac{V X K_{ow} f_L}{Q_a 1000 \rho_L \theta_c} \tag{12}$$

$$S = \frac{V Q_{air}}{Q_a V} 6.18 * 10^{-5} H_c^{1.045} \tag{13}$$

$$B = \frac{V}{Q_a} K^{1} X \tag{14}$$

and, where

REM_{sp}, REM_{st}, REM_{b}, REM_{e} = percent removals of the substrate by sorption, stripping, biotransformation and effluent mechanisms, respectively.

3) The influent substrate is soluble and its concentration is constant.

4) Sorption, biodegradation, stripping and removal with effluent flow are the only significant removal mechanisms.

5) Sorption, biodegradation and stripping occur independently of each other and their effects can be summed.

6) Volatilization, adsorption, and biodegradation losses from other parts of the activated-sludge treatment facility are not significant.

These assumptions are discussed in more detail in Section 4.1.2.1 of this report. The discussion is equally valid for the Blackburn et al. model, and will not be repeated here.

Blackburn et al. make use of a first-order stripping rate equation (Equation 4 in Table 4-4). The values 1.045 and 6.18×10^{-5} are fitted power function constants, which were fit using eleven data points. The authors claim that the equation is accurate in pure water for compounds with Henry's law constants ranging over four orders of magnitude. When "dirty" water is used, (which more accurately describes water at activated sludge facilities), variations from the pure water values as large as 50 percent can result. The use of Equation 4 assumes that diffused-air stripping is a single-stage equilibrium process. In addition, the model assumes that volatilization across the surface of the tank is insignificant and that the inlet gas contains negligible quantities of the compound being modeled.

Blackburn et al. have shown that sorption reaches equilibrium very quickly for many compounds. They conclude that for completely-mixed reactors with a hydraulic retention time of several hours, sorption of specific compounds is an equilibrium process. The authors mention that the equilibrium assumption may not be valid for plug-flow regimes or for chemicals with a high octanol-water partition coefficient. While their research indicates that a Langmuir isotherm describes the sorption process well, they reject the use of the Langmuir equation because of the difficulty in estimating the Langmuir parameters. Instead they propose a linear equation (Equation 5 in Table 4-4) derived in terms of the octanol-water partition coefficient, the values for which are available in the literature. Some assumptions associated with the development of Equation 5 are:

1) Partitioning occurs between the lipophilic fraction of the biomass and water (i.e., sorption onto non-biological solids is not considered).

2) Desorption is not considered.

3) The biological lipids have the same density as n-octanol.

4) Partitioning is passive. That is, no biochemical binding or active cellular transport occur.

5) The aqueous phase concentrations are in a range for which a linear sorption relationship is valid.

In developing the biotransformation rate equation (Equation 6 in Table 4-4), Blackburn et al. treat the entire biomass as a single, non-conservative reactant, instead of considering only the fraction of the total population capable of degrading a specific compound. Before Equation 6 can be used, the concentration of biological solids in the reactor, X, which is a function of the TOC available, needs to be determined. The concentration of biological solids can either be measured or calculated using Equations 1 and 2. Equations 1 and 2 are derived from conventional empirically-developed relationships for growth and non-specific substrate utilization.

The use of Equation 6 to calculate the biotransformation rate assumes that oxygen is not limiting and Monod kinetics can be simplified to a first-order relationship. The authors point out that the Monod relationship is generally preferred by researchers because it describes the change from a first-order to a zero-order biotransformation rate as substrate concentration increases. However, because the estimation of the Monod parameters requires extensive laboratory study and also because most compounds of concern are present at low concentrations in activated-sludge facilities, the first-order relationship is included in their model.

4.1.3.2 Input Requirements--

The input parameters which need to be specified are:

1) The volume of the aeration tank (V)

2) The influent flow rate to the tank (Q_a)

3) The gas volumetric flow rate (Q_{air})

4) The influent concentration of TOC (T_{ao} in Equation 2)

5) The influent concentration of the specific compound (C_{ao} in Equations 3 and 7)

6) The growth yield coefficient for TOC ($\bar{Y}$)

7) The microorganism decay coefficient for TOC (k_d)

8) The TOC utilization rate constant (K^1 in Equation 1)

9) The compound utilization rate constant (K^1 in Equations 6, 7, and 14)

10) The mean cell residence time (θ_c)

11) The lipid weight fraction (f_L)

12) The density of lipids (ρ_L)

13) The octanol-water partition coefficient (K_{ow})

14) Henry's law constant (H_c)

Many of these parameters are difficult to estimate without laboratory analysis. The authors present four values each for Y, k_d, and K^1 in terms of TOC based on laboratory work using four compounds. The results are shown in Table 4-5.

The authors also present four specific compound utilization rate constant values (L/mg-day). These are: Phenol $> 7.61 \times 10^{-1}$, Toluene > 2.54, Aniline $> 6.70 \times 10^{-1}$, Pentachlorophenol 0.0.

TABLE 4-5. BIOKINETIC CONSTANTS IN TERMS OF TOC

Compound	Growth yield coefficient, Y (mg MLSS/mg TOC)	Microorganism decay constant, k_d (hr^{-1})	Substrate utilization rate constant, K^1 (L/mg-hr)
Phenol	0.68	3.33×10^{-3}	6.99×10^{-5}
Toluene	0.84	1.25×10^{-3}	6.67×10^{-5}
Aniline	1.51	4.17×10^{-3}	5.24×10^{-5}
Pentachlorophenol	1.33	4.58×10^{-3}	4.56×10^{-5}

Values for other compounds need to be derived from laboratory studies. The biotransformation rate parameters should be selected with care, because the model is most sensitive to variations in these parameters.

4.1.3.3 Output Description--

The solution to this model occurs in three stages. First, Equations 1 and 2 in Table 4-4 are used to calculate the concentration of biological solids, X, in the reactor. Then the value of X is used, with the appropriate input data, to solve for the steady-state concentration of the specific compound, C_{ae}, in the reactor, using Equation 7. Once the value of C_{ae} is known, Equations 4 through 6 can be solved to determine the rates at which the compound is stripped, adsorbed, and biodegraded. The authors also present equations which can be used to estimate the percent of the influent specific compound which is adsorbed, stripped, biodegraded, or remains in the effluent (see Equations 8 through 14 in Table 4-4).

4.1.3.4 Resource Requirements--

The mathematical model is easily solved using a calculator. Obtaining accurate input data either requires application to a site which has already been extensively studied or requires the use of laboratory studies.

4.1.3.5 Ease of Use--

The model itself is not complex. However, some of the input, particularly the biotransformation rate parameters, can not be obtained without experimentation. The authors suggest that the predictive equations can be used by assigning probable values for the parameters from the literature, along with a reasonable range of values. This allows estimation of how removal by the different mechanisms may range in the "real world."

4.1.3.6 Previous Applications--

The authors present an example calculation using their model. They also found good agreement when they compared results using "most-probable" values in their model with results from their laboratory studies. They also state that their results agree with general findings at full-scale treatment facilities.

4.1.3.7 Availability/Documentation--

The model and related research are described in Blackburn and Troxler (1984), Blackburn et al. (1985) and Blackburn (1987).

4.1.4 The Hwang Model

4.1.4.1 Summary--

Hwang (1981) uses laboratory data to determine the best equations to describe biodegradation kinetics, volatilization and adsorption on sludge in an activated-sludge aeration tank. The tank acts as a continuous-flow, completely mixed unit which is mechanically agitated. By writing a material balance around the aeration tank and including selected kinetic equations for biodegradation, volatilization, and adsorption, Hwang develops a steady-state mathematical model of the fate of a specific compound in the tank. A simplified version of the model, in which adsorption is not considered, is also presented. The important equations in Hwang's model are listed in Table 4-6. A brief discussion of the equations follows.

The biodegradation rate equation (Equation 1 in Table 4-6) uses Grau kinetics to describe the removal mechanism. Before selecting this equation, Hwang used data from four sources to test four different kinetic models (first-order, Monod, Grau, and Hwang). The Grau kinetic model best fits the data. Hwang rejects the use of a first-order relationship because it can not predict the decrease in removal efficiency with increase in influent substrate concentration which has been observed in single-component batch experiments. While Hwang is right about this limitation of first-order kinetics, in multi-component systems in which the volatile organics of interest are present at low concentrations and are non-interactive, first-order kinetics can

TABLE 4-6. IMPORTANT EQUATIONS IN THE HWANG MODEL

1) Biodegradation reaction rate

$$-\frac{dS}{dt} = K_{1(s)}\, X \left[\frac{S}{S_o}\right] \tag{1}$$

where

S = substrate concentration (μg/L)

t = time (days)

X = biomass concentration (μg/L)

$K_{1(s)}$ = rate constant (1/day)

S_o = initial substrate concentration (μg/L)

2) Volatilization reaction rate

$$-\frac{dS}{dt} = \left[(K_a)_T \frac{A_T}{A} + (K_a)_C \frac{A_C}{A}\right] S \tag{2}$$

where

A_T = turbulent surface area (m^2)

A_C = convective surface area (m^2)

A = total surface area (m^2)

$(K_a)_T$ = rate constant for turbulent area (1/day)

$(K_a)_C$ = rate constant for convective area (1/day)

3) Concentration of compound adsorbed on sludge

$$[B.S] = \frac{K_1\, X'\, S}{1 + K_1\, S + K_T\, S_r} \tag{3}$$

where

$[B.S]$ = concentration of substrate on sludge (μg/L)

K_1, K_T = adsorption constants

X' = maximum amount of substrate adsorbed (μg/L)

S_r = concentration of total substrate minus the substrate under consideration, S (μg/L)

TABLE 4-6. IMPORTANT EQUATIONS IN THE HWANG MODEL (continued)

4) Material balance

$$Q_F \; S_o - (Q_F - Q_W)S_e = \frac{K_{1(s)}X \; S_e}{S_o} V + K_a \; S_e \; V + Q_W \frac{K_1 \; X' \; S_e}{1 + K_T S_r + K_1 S_e} \qquad (4)$$

where

Q_F = fresh feed flow (L/day)
Q_w = waste sludge flow (L/day)
S_e = effluent substrate concentration (μg/L)
V = volume (L)
K_a = $(K_a)_T \; A_T/A + (K_a)_C \; A_C/A$

5) Fresh feed flow

$$Q_F = \frac{Q}{1 + r} \qquad (5)$$

where

Q = total flow (L/day)
r = recycle ratio (Q recycled/Q_F)

6) Steady-state reactor concentration with adsorption

$$S_e = \frac{- \; b + \sqrt{b^2 + 4a \; S_o \; (1 + K_T \; S_r)}}{2a} \qquad (6)$$

where

$$b = 1 - K_1 \; S_o + K_T \; S_r + \frac{K_{1(s)} \; X}{S_o} (1 + r) \; t_c \; (1 + K_T \; S_r)$$
$$+ K_a \; (1 + r) \; t_c \; (1 + K_T \; S_r) + K_1 \; X' \; (1+r) \frac{Q_w}{Q}$$

$$a = K_1 \; (1 + (1 + r) \frac{K_{1(s)} \; X}{S_o} \; t_c + (1 + r) \; K_a \; t_c)$$

t_c = hydraulic residence time (days)

TABLE 4-6. IMPORTANT EQUATIONS IN THE HWANG MODEL (concluded)

7) Steady-state reactor concentration without adsorption

$$S_e = \frac{S_o}{1 + \frac{K_{1(s)}\ X}{S_o} (1 + r)\ t_c + (1 + r)\ K_a\ t_c} \tag{7}$$

adequately describe the system (Weber et al., 1986). The advantage of Equation 1 is that it can be used over a wider range of concentrations. The Grau kinetic model assumes a sufficient oxygen supply is available for biological activity (i.e., oxygen is not limiting).

The volatilization rate equation (Equation 2 in Table 4-6) is based on Fick's law of diffusion. The mass transfer coefficient is an area-averaged value for zones of turbulence and convection. Both the turbulent and the convective rate constant are based on two-phase resistance theory and can be estimated using equations presented in Section 2. Hwang mentions that the liquid-phase resistance is often controlling for volatile compounds. An assumption made in developing Equation 2 in Table 4-6 is that reactions in the subsurface do not affect mass transfer at the surface.

Hwang derives a Langmuir-type multi-component adsorption equation to describe the equilibrium concentration of a specific compound on the waste sludge (Equation 3 in Table 4-6). According to Hwang, equilibrium between the concentration of adsorbed priority pollutants and the liquid substrate concentration can be assumed because most of the sludge is recycled back into the aeration tank. Equation 3 is relatively complex and requires knowledge of two adsorption constants.

The overall mass balance equation developed by Hwang is represented in Equation 4 of Table 4-6. The six assumptions made in developing the Namkung-Rittmann overall mass balance equation (see Section 4.1.2) also apply to the development of Hwang's model.

4.1.4.2 Input Requirements--

Without adsorption, the input parameters which need to be specified by the user are:

1) The hydraulic residence time (t_c)
2) The initial substrate concentration (S_o)
3) The biomass concentration (X)
4) The biodegradation rate constant ($K_{1(s)}$)
5) The turbulent-area volatilization rate constant ($(K_a)_T$)
6) The convective-area volatilization rate constant ($(K_a)_C$)
7) The recycled flow rate (Q recycle)
8) The fresh-feed flow rate (Q_F)
9) The total, turbulent, and convective surface areas (A, A_T, A_C)

With adsorption, all the input parameters listed in (1) through (9) are needed, as well as:

10) The total influent flow rate (Q)

11) The waste sludge flow rate (Q_w)

12) The maximum amount of adsorbed substrate (X')

13) The concentration of the total substrate minus the compound under consideration (S_r)

14) The adsorption constant for the specific compound (K_1)

15) The adsorption constant for the rest of the substrate (K_T)

The Grau kinetics biodegradation rate constant ($K_{1(s)}$) needs to be developed from laboratory data. Hwang has done this for many organics of concern, but the table listing these values is not included in Hwang (1981). When contacted, Hwang was not able to provide the tables for inclusion in this report. Because the Grau kinetic model is not widely used, it is extremely difficult to locate appropriate values in the literature. Likewise, the two adsorption constants (K_1 and K_T) and the maximum adsorbed concentration (X') need to be determined using adsorption data. While Hwang has done this for many organics, the values are not available. Another problem with calculating the equilibrium concentration of the compound adsorbed on the sludge, using Equation 3 as it is written, is that the input parameter S_r, which is the concentration of the total substrate in the liquid minus the concentration of the specific compound in the liquid, can not be known without direct measurement. The concentration of the specific compound in the liquid, S, which because of complete mixing is assumed to equal the effluent concentration, S_e, is the unknown variable which is solved for in Equations 6 and 7.

4.1.4.3 Output Description--

Equation 6 shows the quadratic equation which represents the steady-state substrate concentration in the reactor in Hwang's model. This value for a specific compound must be calculated before the fate of that compound can be determined. As it is written, Equation 6 can not be solved unless the value of S_r is measured beforehand. If S_r is measured, S_e can easily be measured at the same time. Thus, Equation 6 would not be needed at all and the various kinetic equations could be used directly. Hwang's model with adsorption can be used, however, if the expression ($K_T S_r + K_1 S_e$) in last term of the material balance in Equation 4 is replaced by the single parameter, S_e. Hwang makes this substitution in his paper after the model equations have been presented, but with no discussion. If the substitution is made, Equation 4 can be rearranged to yield an equation for the substrate concentration in the reactor.

As has been discussed elsewhere, adsorption is an unimportant removal mechanism for many organics. If adsorption can be neglected in the material balance, Hwang's model is greatly simplified. The substrate concentration in the reactor can be readily calculated from Equation 7. The greatest uncertainty associated with using Equation 7 is in estimating the biodegradation rate constant ($K_{1(s)}$).

Once the substrate concentration has been calculated, the fate of the compound can be determined by applying the specific kinetic relationships in Equations 1 through 3 when adsorption is considered, or Equations 1 and 2 otherwise.

4.1.4.4 Resource Requirements--

Once the input data have been specified, this model can be solved using a calculator. It can also be programmed for use on a computer.

4.1.4.5 Ease of Use--

Hwang's model with adsorption included is complex and can not be easily used without making the substitution discussed above. It is better to use Hwang's model only when adsorption can be neglected. Then if the biorate constant is known, it is a simple model to apply.

4.1.4.6 Previous Applications--

Hwang used laboratory data to select the kinetic relationships used in his model. He does not apply the unified model to a specific site, however. No applications by other researchers are known.

4.1.4.7 Availability/Documentation--

The model is described in Hwang (1981) and in Breton et al. (1984). Unfortunately, the table of kinetic constant values, which would be extremely useful, is not included in the model documentation, nor is it available directly from the author. It should be noted that a typographical mistake is included in the development of the equations as they are presented in Hwang (1981) and Breton et al. (1984).

4.1.5 The NCASI Model (NOCEPM)

4.1.5.1 Summary--

The National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI) has developed a screening model which predicts the intermedia distribution of organics in either an activated-sludge aeration tank or an aerated stabilization basin (ASB). The model, which is named the NCASI Organic Compound Elimination Pathway Model (NOCEPM), is written in BASIC for use on an IBM personal computer or a compatible computer. The development of the mathematical equations in the model is described in a NCASI technical bulletin (1986) and in Barton (1987). Appendices in the bulletin contain a user's manual and a source code listing for NOCEPM.

The four removal pathways considered in NOCEPM are stripping by either surface or subsurface aeration, natural volatilization, adsorption, and biodegradation. The model is intended for screening purposes in determining the fate of specific compounds. As a result, the model has been formulated so it can be used with data available in the literature.

The important equations used in the NCASI model are listed in Table 4-7. Note that the removal rates are expressed in terms of mass per volume per day. These equations and the assumptions associated with them are discussed below. The development of the overall material balance (Equation 1 in Table 4-7) assumes:

1) The basin being modeled is a completely-stirred reactor. While municipal activated sludge units are often designed for plug flow, the activated-sludge units used by the paper industry, for which this model was developed, can be described as completely-mixed reactors.

2) Steady-state conditions exist. In reality, the concentration of the specific compound may vary considerably over short times.

3) The only significant removal mechanisms are stripping, passive volatilization, adsorption, and biodegradation. Stripping can occur either at the interface of diffused air bubbles in the tank or the interface of water droplets in the spray produced by surface aerators.

4) The removal mechanisms are independent and can be summed to estimate total removal. A brief discussion of this assumption is given in Section 4.1.2.

5) A single reactor is modeled. Thus, loss, of the organic compound from other parts of the treatment facility is assumed to be insignificant. This assumption may underestimate total emissions slightly.

In developing the stripping equations, a number of simplifying assumptions are made:

1) Two-film theory is used to estimate the overall mass transfer coefficient.

2) The liquid-phase transfer coefficient is related to the total oxygen mass transfer coefficient by means of a proportionality coefficient. This is because the gas-phase resistance in oxygen transfer is not significant and because the proportionality coefficient is a function of the relative diffusivities of the compound and oxygen in water only.

3) The exponent used in calculating the proportionality coefficient is assumed to be 0.6 for all compounds. This is an approximation based on analysis of measured values for different compounds.

TABLE 4-7. IMPORTANT EQUATIONS IN THE NCASI MODEL (NOCEPM)

1) Overall model equation

$$\frac{dC_{Li}}{dt} = 0 = \frac{Q}{V} (C_{Li,I} - C_{Li}) - r_s - r_v - r_a - r_b \qquad (1)$$

where

$C_{Li,I}, C_{Li}$ = influent and effluent concentration of compound i (mg/m^3)

Q = volumetric liquid flow (m^3)

V = aeration basin volume (m^3)

r_s = stripping removal rate (mg/m^3-hr)

r_v = volatilization removal rate (mg/m^3-hr)

r_a = adsorption removal rate (mg/m^3-hr)

r_b = biodegradation removal rate mg/m^3-hr)

2) Stripping rate

a) Stripping from surface aeration

$$r_s = K_L^s a_i \, C_{Li} \qquad (2)$$

where

$K_L^s a_i$ = overall mass transfer coefficient of compound i (1/hr)

b) Stripping from subsurface aeration

$$r_s = \frac{Q_G}{V} H_c \, C_{Li} \, (1 - e^{-\theta}) \qquad (3)$$

where

Q_G = gas flow rate (m^3/hr)

H_c = dimensionless Henry's Law constant

$\theta = \frac{K_L^s a_i \, V}{H_c \, Q_G}$

c) H_c is calculated as:

$$H_c = H/RT \qquad (4)$$

TABLE 4-7. IMPORTANT EQUATIONS IN THE NCASI MODEL (NOCEPM) (continued)

where

H = Henry's Law constant (atm-m^3/mol)
R = Universal Gas constant (atm-m^3/mol-°K)
T = absolute temperature (°K)

d) $K_L^s a_i$ is calculated as:

$$\frac{1}{K_L^s a_i} = \frac{1}{\psi\ K_L a_{O_2}} + \frac{1}{20\ H_c\ \psi\ K_L a_{O_2}} \qquad (5)$$

where

ψ = transfer rate proportionality coefficient
$K_L a_{O_2}$ = mass transfer coefficient of oxygen (1/hr)

e) $K_L a_{O_2}$ is calculated as:

$$K_L a_{O_2} = \frac{454\ N_o\ HP\ \alpha\ \theta^{T-20}}{C_s^*\ V} \qquad (6)$$

where

N_o = standard oxygen transfer rate (lbs. O_2/HP-hr)
HP = total aeration horsepower (HP)
α, θ = oxygen transfer correction factors (-)
C_s^* = dissolved oxygen saturation concentration at 20°C (mg/l)
V = basin volume (10^6 liters)

3) Volatilization rate

$$r_v = \left[\frac{1}{\psi\ K_L^v a_{O_2}} + \frac{1}{H_c\ 700\ \left[\frac{18}{MW}\right]^{1/4}\ V_w\ \frac{24}{100\ Z}}\right]^{-1} C_{Li} \qquad (7)$$

where

MW = compound molecular weight (g/mol)
V_w = ambient wind velocity (m/s)
Z = basin depth (m)
$K_L^v a_{O_2}$ = oxygen surface reaeration rate (1/day)

TABLE 4-7. IMPORTANT EQUATIONS IN THE NCASI MODEL (NOCEPM) (concluded)

4) Adsorption rate

a) $$r_a = \frac{SP\ K_p\ C_{Li}}{V} \qquad (8)$$

where

SP = rate of sludge removal (kg/hr)

K_p = adsorption partition coefficient (L/g)

b) K_p is calculated as:

$$\log K_p = 0.67 \log K_{ow} - 2.61 \qquad (9)$$

where

K_{ow} = n-octanol-water partition coefficient (L/g)

5) Biodegradation rate

$$r_b = k_2\ X\ C_{Li} \qquad (10)$$

where

k_2 = second order rate constant (L/mg-X per hr)

X = volatile suspended solids (mg/L)

6) Results in terms of percent removal

$$\frac{C_{Li,I} - C_{Li}}{C_{Li,I}} = \frac{r_s' + r_v' + r_a' + r_b'}{\frac{Q}{V} + r_s' + r_v' + r_a' + r_b'} \qquad (11)$$

where

$r' = r/\ C_{Li}$

4) The ratio of gas-phase to liquid-phase mass transfer coefficients, (k_g/k_l), which has been shown to decrease with increasing basin turbulence, is assigned a value of 20, instead of the value of 150 reported for natural water surfaces. The choice of 20 as the ratio value is based on the research of others.

5) For surface-aerated basins, the concentration of the compound in the air is assumed to be zero. Thus no ambient air saturation model is incorporated. As long as the aeration basin is uncovered, it is reasonable to assume that atmospheric turbulence will keep compound concentrations in the air small enough to neglect.

6) For diffused-air systems, partial saturation of the bubbles is assumed.

The extent of saturation is considered in determining the stripping rate (Equation 2b.). The equation is based on the work of Roberts et al. (1984) and Matter-Mullër et al. (1981).

The volatilization rate equation was developed assuming:

1) The two-film resistance model for mass transfer applies.

2) The liquid-phase transfer coefficient is related to the total oxygen mass transfer coefficient by means of a proportionality coefficient. The grounds for making this assumption were stated above.

3) The natural oxygen reaeration rate across the basin surface is assumed to be 0.5 day^{-1}. This is based on reported values for rivers and streams.

4) The gas-phase transfer coefficient is related to the wind velocity, the molecular weight of the compound, and the depth of the basin. This relationship is shown in the second term on the right-hand side of Equation 3.

Adsorption onto biological solids in the basin is modeled by assuming:

1) Adsorption occurs so rapidly that equilibrium conditions exist.

2) Equilibrium concentrations are expressed by a linear isotherm. (The inclusion of Freundlich and Langmuir isotherms was intended in the model design, but has not been implemented in the current version of the code.

3) If the equilibrium partition coefficient is not known, it is approximated using a linear relationship between the logs of the partition coefficient and the octanol-water coefficient.

4) The extent of removal by adsorption is determined by the rate of sludge removal and the equilibrium partition coefficient.

5) The value of the partition coefficient is assumed to be independent of the concentration of solids.

6) The sorptive capacity of the wasted solids and the effluent suspended solids is assumed to be the same.

Use of the biodegradation rate equation assumes that:

1) The compounds do not inhibit biological activity.

2) The biodegradation rate is second-order.

3) A sufficient oxygen supply is available.

4.1.5.2 Input Requirements--

The input parameters which need to be specified by the user are:

1) The wastewater flow rate (Q)

2) The basin volume (V)

3) The basin temperature (T)

4) The basin surface area (A)

5) The mixed-liquor volatile suspended solids (MLVSS) concentration (X)

6) The effluent total suspended solids

7) The wasted solids

8) The type of aeration system used

9) The standard oxygen transfer efficiency (N_o)

10) Total horsepower (HP)

11) Gas flow (Q_G)

12) Average ambient wind velocity (V_w)

13) Henry's law constant (H)

14) Compound diffusivity in water (D_i)

15) Surface reaeration rate ($K_L^V a_{O_2}$)

16) Compound molecular weight (MW)

17) The compound octanol-water coefficient (K_{ow})

18) The biodegradation rate constant (k_2)

19) The compound influent concentration ($C_{Li,I}$)

Values for parameters 13 through 18 are provided in an online data-base for 36 organic compounds. For other compounds, most of the needed data can be found readily in the literature. If the compound diffusivity in water is not available, Barton (1987) provides further assistance in estimating it. He also suggests that a default value of 0.5 day^{-1} be used for the surface reaeration rate. The biodegradation rate constant is often not known. Thus, the computer model provides the option of estimating a compound's biodegradation rate as either high, medium, or low.

The input data are easily entered using five separate screens which specify the data to be entered.

4.1.5.3 Output Description--

Model output is written to the screen and consists of three groups of information. The first screen summarizes the model input, so the user can verify that it was entered correctly. The next screen lists the values of parameters which are calculated by the model, such as the solids partition coefficient and the oxygen transfer rate. The same screen lists the reaction rates for passive volatilization, stripping, sorption, and biodegradation (Equations 2 through 5 in Table 4-7). The reaction rates are expressed in terms of a value which has not been multiplied by the concentration. The final output screen shows the results expressed as percent of influent concentration removed by means of each of the four pathways and the liquid-phase effluent. Equation 6 in Table 4-7 can be used to obtain these results. The percent of the compound adsorbed is broken down into adsorption onto effluent suspended solids and onto wasted solids. These values are calculated based on the rate of solids removal, which is an input parameter. Emission rates in pounds per year are also given. Total percent removal and total emission rates are calculated differently. Total percent removal does not include adsorption onto effluent solids, because adsorption does not remove the compound from the effluent stream. The total emission rate includes passive volatilization, stripping, and adsorption rates only, because biodegradation does not cause the emission of a compound from the facility.

4.1.5.4 Resource Requirements--

The computer program is designed for use on an IBM personal computer or compatible computer. The equations in Table 4-7 can also be solved by hand. Because the model is meant for screening purposes only, most of the input data can be found in the literature.

4.1.5.5 Ease of Use--

The interactive software and built-in data base make this an easy model to use.

4.1.5.6 Previous Applications--

The model was used to screen four compounds potentially present in the pulp and paper industry wastewater. For two of the compounds, predicted results were compared with data from activated-sludge units and with literature values. The model results were considered adequate.

4.1.5.7 Availability/Documentation--

NOCEPM is available to the paper industry and to the Environmental Protection Agency. More information can be obtained by contacting the National Council of the Paper Industry for Air and Stream Improvement, Inc., 260 Madison Avenue, New York, NY, 10016.

4.1.6 The Environmental Protection Agency Models

In U.S. EPA (1987b), equations are presented which can be used to predict emissions from both mechanically-aerated and diffused-air systems. The mathematical models, which can be used for either surface impoundments or activated-sludge aeration tanks, are described in Section 5.4.2, 5.4.3 and 5.4.4. The model equations, shown in Tables 4-11 for mechanically-aerated systems and in Table 4-13 for diffused-air systems, are identical for both activated-sludge units and surface impoundments. Only the values of the input parameters will differ. Activated-sludge tanks differ from surface impoundments by having (U.S. EPA, 1987b):

1) a higher biomass concentration
2) a smaller surface area
3) a shorter retention time
4) a greater turbulent area
5) a smaller fetch to depth ratio

The mathematical models have been incorporated into a Lotus 1-2-3 spreadsheet, called CHEMDAT6, which is included in U.S. EPA (1987b) on a floppy diskette. Both a general description of CHEMDAT6 and a specific description of the aerated and non-aerated impoundment models in CHEMDAT6 are presented in Section 5.4.5. The reader is referred to Sections 5.4.2 through 5.4.5 for descriptions of these models.

4.1.7 Other Activated-Sludge Models

Two models have been developed by Freeman for the activated-sludge process. Both models have been reviewed in detail in Breton et al. (1984). Brief summaries are presented here. The first model (Freeman, 1979) simulates the fate of an organic pollutant in a surface-aerated tank. According to Breton et al. (1984), the only major difference between it and the Hwang (1981) model with no adsorption (Section 4.1.4) is in the consideration of the biodegradation kinetics. Freeman includes material balances for the substrate, oxygen, and biomass in his model. As a result, the active biomass is no longer an input parameter and the assumption that oxygen is in sufficient supply is not needed. Freeman (1982) modified the first model to account for diffused aeration. This second model is identical to the earlier surface-aeration model, except for the calculation of mass transfer. Both models require the solution of three simultaneous non-linear equations by iteration, and therefore, should be programmed on a computer. In addition, the biokinetic data are difficult to obtain.

Weber et al. (1987) model the removal of organics in a completely-mixed, steady-state activated-sludge system. Their mass balance equation includes first-order volatilization and biodegradation rate equations. They present a linear equilibrium sorption equation, but do not include it in their mass balance for the system. The formulation of the mass balance and the kinetic relationships is similar to others discussed in this report.

Roberts et al. (1984) present equations which can be used to calculate the fraction of a wastewater constituent removed by either surface-aeration or subsurface sparging. Sorption or biotransformation are not included in the models. Therefore, the equations will tend to overestimate emissions from an activated-sludge facility and are only appropriate for "worst-case" scenarios.

Rittmann et al. (1988) present a general mass-balance model which includes convection, biodegradation, adsorption, and volatilization as mechanisms affecting the fate of organics. It can be applied to both aerobic and anaerobic systems. The word "general" must be stressed. The model is not intended for activated-sludge facilities specifically and many system-specific details are not included.

4.2 POWDERED ACTIVATED CARBON TREATMENT (PACT^{tm})

4.2.1 Modeling Approaches

As was discussed in Section 3.2.2, the addition of powdered activated carbon (PAC) to activated-sludge aeration tanks or to sequencing batch reactors improves the efficiency of these facilities in removing hazardous compounds from the wastewater. Weber et al. (1987) found that the addition of 100 mg/L of PAC to bench-scale units resulted in approximately equal percent reductions in effluent and off-gas concentrations of poorly-degradable volatile compounds. Although the addition of PAC did not significantly affect the steady-state removal of readily biodegradable compounds, it did improve removal during periods of acclimation. Clearly, adsorption onto PAC is a removal mechanism which needs to be incorporated into models of the PACT process. Three different approaches to modeling adsorption in a PACT facility have been presented in the literature.

Garcia-Orozco et al. (1986) compare the performance of experimental activated-sludge and PACT units in the presence of 4,6-dinitro-o-cresol. They develop an empirical expression which estimates overall PACT effluent concentration as a function of the effluent concentration at an identical activated sludge tank, and the carbon dosage. Neither biosorption nor stripping are considered in the equation and the empirical constants must be determined in the laboratory.

The authors also present a model for the removal of a specific priority pollutant when using the PACT process. Removal depend on a zero-order biodegradation term and an adsorption term. Adsorption is modeled as the product of the carbon dosage and the carbon adsorption capacity. The carbon adsorption capacity needs to be determined experimentally, assuming equilibrium conditions. The authors found different values for this parameter using batch tests and experimental reactor results. They suggest different adsorption competition conditions caused the discrepancy. As a result, the carbon adsorption capacity would be a difficult parameter to identify for full-scale PACT facilities. In addition, the Garcia-Orozco et al. model is not useful in the context of this report, because air emissions are assumed negligible.

Takács (1986) describes a dynamic mathematical model of the PACT process. The model, which has been verified for both batch and continuous-flow conditions, has been coded for use on a personal computer. The model describes adsorption and the biological processes of biodegradation of carbonaceous material, microbial growth, and oxygen utilization. Because neither volatilization, nor the ability to model the fate of a specific compound are included in the model, it is not discussed in-depth in this report. However, the method used by the authors to model PAC adsorption is relevant.

The authors assume that adsorption is an instantaneous equilibrium reaction which can be predicted by means of a Langmuir isotherm. The Langmuir isotherm is described in Section 2.4.1.2. Because the reaction is assumed instantaneous, the influent concentration of non-biodegradable organics is reduced by the amount adsorbed. The effect of the PAC on the dissolved substrate is modeled by increasing the substrate maximum utilization rate. Finally it is assumed that no adsorption on suspended solids occurs.

Weber et al. (1987) found that PAC adsorption data from bench-scale PACT units adhered to the Freundlich isotherm model, described in Section 2.4.1.1. They present values for the two Freundlich isotherm coefficients for nine target compounds. Although the authors present a model of the fate of toxic organics in an activated sludge system and discuss the addition of PAC, they do not develop a model which describes the PACT process.

The three different approaches to describing adsorption in a PACT system share a common assumption that the absorbed compound concentration is in equilibrium with the liquid concentration. However, Schultz and Keinath (1984) experimentally observed lower adsorbed phenol concentrations than would be predicted on the basis of adsorption equilibrium. They suggest that the biomass, which can use the carbon particles as a support medium, impedes mass transfer to the PAC surface, making the use of equilibrium isotherms invalid. Complex mass transfer models may be needed.

Given the current lack of models which consider both air emissions and adsorption in the PACT system, two approaches are suggested for estimating emissions of volatile organics. Conservative estimates can be made by ignoring adsorption and using any appropriate model described in Sections 4.1 or 4.3. Otherwise, in an approach similar to that of Takács (1986), the equilibrium adsorption concentration can be calculated initially and subtracted from the influent concentration. The reduced influent concentration can then be used in the available activated sludge or sequencing batch reactor models.

4.3 SEQUENCING BATCH REACTOR MODELS

4.3.1 Introduction

As was described in Section 3.2.3, sequencing batch reactors (SBR) normally operate in a five-stage cycle. Air emissions are most likely during the first and second steps, called the fill and react steps, because aeration and mixing occur during those stages. For each of the two steps, the methods of estimating the magnitude of emissions are discussed below.

Some volatilization may occur from the quiescent surface of the tank during step 3, the settling stage. The magnitude of emissions is likely to be small because the desired degree of remediation will have already been achieved and because no mixing and aeration occur. The settling step can be modeled, however, using the equations described in Section 4.3.3.1. If that model is used, the overall volatilization mass transfer coefficient must be recalculated using correlations developed for quiescent surfaces.

4.3.2 The Fill Step

During the fill step, the volume of waste in the tank is a function of time. Volatilization across a turbulent surface and biodegradation both contribute to removal of contaminants in the waste. Volatilization can also occur from the stream of inflowing water, if the inlet is located above the water level. Adsorption occurs, but is often assumed negligible for volatile organics. Orhon et al. (1986) present a mass balance equation for the fill phase of a SBR. Biodegradation is the only removal mechanism modeled and utilization of the soluble substrate is assumed to be limited by microbial growth.
The mass balance for substrate removal is:

$$\frac{ds}{dt} = \frac{Q(S_o - S)}{V_o + Qt} - r_s \tag{1}$$

where

Q = influent flow rate (L^3/t)

S_o = influent substrate concentration (M/L^3)

V_o = the initial volume in the reactor (L^3)

S = substrate concentration in the reactor (M/L^3)

r_s = substrate utilization rate (M/L^3t)

The authors use the Monod equation to represent the kinetics of total substrate utilization. A different kinetic relationship, such as a first-order equation, can be substituted, however, to simulate the fate of a single compound present at low concentrations. In order to estimate volatilization, Equation 1 needs to be further modified as:

$$\frac{ds}{dt} = \frac{Q(S_o - S)}{V_o + Qt} - r_s - r_v \qquad (2)$$

where

r_v = volatilization rate (M/L^3t)

A kinetic model of volatilization from a turbulent surface needs to be identified. One such kinetic equation is discussed in Section 4.4.3. After substituting the two kinetic expressions into Equation 2, the equation must be integrated to yield an expression for substrate concentration as a function of time.

An easier and more conservative approach it to make several simplifying assumptions. These are:

1) no biodegradation occurs during the fill stages
2) the surface area of the tank is constant
3) the concentration in the influent waste is constant
4) the concentration of the chemical in the tank can be approximated by the influent concentration

The justification for the last assumption is that the tank is well-mixed because of the turbulent influent flow and that the tank is continuously supplied with fresh influent waste. These assumptions will overpredict true emissions, but allow the use of a very simple equation.

$$E = K_v A C_o \qquad (3)$$

where

E = the volatilization rate (M/t)

K_v = the overall mass transfer coefficient (L/t)

The overall mass transfer coefficient can be approximated with correlations developed for turbulent surfaces and described in Section 2.

A method of estimating emissions from the stream of water flowing into the tank is presented in Section 6.1.2.2. Unlike the application in Section 6.1.2.2, the length of the stream feeding the SBR changes with time. For a rough approximation, the average length of the stream can be used.

4.3.3 The React Step

During the react step, the flow rate is zero (and thus, the volume of waste does not change with time). Equation 2 reduces to:

$$\frac{ds}{dt} = -r_s - r_v \qquad (4)$$

The substrate concentration decreases with time due to volatilization and biodegradation. Two models, which can be used to predict the fate of a compound during the react stage in a surface-aerated SBR, are presented below. The user can construct other models by substituting appropriate kinetic expressions into Equation 3 and integrating.

4.3.3.1 The EPA Model for No-Flow, Surface Aerated Basins--

Equations which describe no-flow conditions in a surface-aerated basin are presented in U.S. EPA (1987b) for a disposal impoundment and are summarized in Table 4-8. The equations are very similar to the equations in Table 4-12, which describe plug flow in a surface impoundment (see Section 4.4.2). Only the final integration constant has changed to reflect the fact that there is no effluent flow. As is true for plug-flow conditions, integration of Equation 1 in Table 4-8 allows prediction of the fate of a compound, but no information about peak removal rates is obtained.

In Equation 1 of Table 4-8, the volatilization rate is assumed to be the product of the concentration, the surface area and an overall mass transfer coefficient value. Individual liquid-phase and gas-phase transfer coefficients are needed to calculate the overall coefficient and can be estimated using equations from Section 2. The authors of U.S. EPA (1987b) use the liquid-phase transfer coefficient equation of Thibodeaux (in Hwang, 1982) and the gas-phase transfer coefficient equation of Reinhardt (1977).

The biodegradation kinetics expression incorporated into Equation 1 is identical to that used in the quiescent surface impoundment model (Section 4.4.2). A description of the kinetic expression is given in Section 4.4.2.1 and will not be repeated here.

The input requirements are listed in Section 4.4.2.2, with the exception that the flow rate is zero. Applying the input parameters to Equations 2 through 5 in Table 4-8, yields information on the average emission rate over the specified time period, as well as the fraction of the compound volatilized, biodegraded, and remaining in the tank.

Example calculations are presented by the authors, but no other applications of the model have been identified.

4.3.3.2 The Environmental Protection Agency Spreadsheet (CHEMDAT6)--

The disposal impoundment model presented in U.S. EPA (1987b) can be used to estimate emissions from a diffused-air SBR during the react and settle stages. That model, modified to take into account mechanical aeration during the react

TABLE 4-8. IMPORTANT EQUATIONS IN THE EPA MODEL FOR A NO-FLOW, SURFACE-AERATED BASIN

1) Rate of compound disappearance caused by biodegradation and volatilization for a single-component system**

$$-\frac{dC_t(V)}{dt} = B\ b_i\ V\ C_t/C_o + K\ A\ C_t \qquad (1)$$

where

C_t = concentration at time t (g/m^3)
t = time (s)
C_o = inlet concentration (g/m^3)
B = biorate constant (g/s per g biomass)
b_i = biomass concentration (g/m^3)
V = volume (m^3)
K = overall mass transfer coefficient (m/s)
A = area (m^2)

2) Equation (1) integrated from $C_t = C_o$ at $t = 0$ to $C_t = C_t$ at $t = t$

$$C_t/C_o = \exp(-B\ b_i\ t/C_o - K\ A\ t/V) \qquad (2)$$

where

C_t/C_o = fraction of compound remaining in the tank

3) Fraction of the compound volatilized for a single-component system**

$$f_{air} = (1 - C_t/C_o)(K\ A)/(K\ A + B\ b_i\ V/C_o) \qquad (3)$$

where

f_{air} = volatilized fraction of the compound

4) Fraction of the compound biodegraded for a single-component system**

$$f_{bio} = (1 - C_t/C_o)(B\ b_i\ V/C_o)/(K\ A + B\ b_i\ V/C_o) \qquad (4)$$

where

f_{bio} = biodegraded fraction of the compound

TABLE 4-8. IMPORTANT EQUATIONS IN THE EPA MODEL FOR A NO-FLOW, SURFACE-AERATED BASIN (concluded)

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5) Average emission rate over the time period

$$E = f_{air} V C_o/t \tag{5}$$

where

E = average emission rate (g/s)

6) Weighting factor for one component of a multi-component system

$$W_1 = B_1 C_{o1} \left[\sum_{i=1}^{n} B_i C_{oi} \right]^{-1} \tag{6}$$

where

W_1 = weighting factor for component 1 (dimensionless fraction)
B_1 = biorate for component 1 (g/s per g biomass)
C_{o1} = inlet concentration of component 1 (g/m^3)
n = number of components in the mixture
B_i = biorate of component i (g/s per g biomass)
C_{oi} = inlet concentration of component i (g/m^3)

** When predicting the fate of one compound in a multi-component system, the biorate constant (B) in this equation should be replaced by the effective biorate constant (B*W), where W is a weighting factor calculated in Equation 6.

stage was discussed in Section 4.3.3.1. A version of the model, which can describe emissions from a quiescent surface during the settle stage and from a diffused-air system during the react stage, has been included by the U.S. EPA in a Lotus 1-2-3 spreadsheet, called CHEMDAT6. CHEMDAT6 is described in Section 4.4.5. Only the application of the disposal impoundment model to a SBR is addressed here. The equations used in CHEMDAT6 to model the settle stage are exactly the same as those shown in Table 4-8. The difference between the quiescent and mechanically-aerated models lies in the choice of correlations to determine the mass transfer coefficient.

Because CHEMDAT6 uses the correlations for a quiescent surface, it can not be used to simulate the react stage of a mechanically-aerated SBR. A user of CHEMDAT6 can estimate emissions from a diffused-air SBR, however. The only additional parameter needed is a value for submerged air flow. The equations which take stripping into account are not shown. The input parameters required to estimate the fate of a compound are: the wind speed, the depth and surface area of the tank, the temperature, the time period, the initial concentration of both the specific compound and the total organics, the active biomass, the total biorate, and for diffused-air systems only, the submerged air flow.

The output provided by CHEMDAT6 consists of the fractions of the compound emitted to the air, biodegraded, and remaining. The estimated yearly emission rate, assuming continuous operation, is also provided. This value is meaningless for application of this model to a SBR.

The use of this model for SBR systems is not discussed in U.S. EPA (1987b). Example calculations for a quiescent disposal impoundment are presented by the authors, but no examples for the diffused-air system are given.

4.4 SURFACE IMPOUNDMENT MODELS

4.4.1 Introduction

Surface impoundments used for bioremediation of organic waste are similar in many ways to activated-sludge aeration tanks. Many of the points discussed in the introduction to activated-sludge models, Section 4.1.1, are valid for surface impoundments as well.

As is the case for activated-sludge units, surface impoundments can experience periods of biological inactivity due to shock loading of toxic chemicals, or a lack of acclimation to a chemical. To model this condition, the biodegradation rate constant in the surface impoundment models should be set to zero.

If the surface impoundments are aerated to promote biological activity, the same equations can be used to predict the fate of compounds in the waste. The values of the input parameters will differ. In general, surface impoundments have lower biomass concentrations and larger surface areas and retention times than activated sludge units. In addition, it can not be assumed that aeration of surface impoundments will result in a completely turbulent surface. It may be necessary to model volatilization from two gas zones--turbulent and quiescent. Even though such systems are only partially mixed, they are modeled as completely-mixed basins for the sake of simplicity.

Aeration is achieved by subsurface diffused aeration or by mechanical agitation. Both types of aeration can be simulated by a computer model developed by Barton (1987) for the National Council of the Paper Industry for Air and Stream Improvement (NCASI) or by models developed by the U.S. EPA (1987b). The U.S. EPA models are also included in CHEMDAT6 (U.S. EPA, 1987b).

Some surface impoundments used for bioremediation, such as waste stabilization ponds, are not aerated. Thus, models which consider emissions from quiescent surfaces are also needed. Either plug-flow or completely-mixed conditions can exist in quiescent surface impoundments. The U.S. EPA (1987b) presents models which consider both types of flow in quiescent impoundments. The U.S. EPA (1987b) model of a completely-mixed, quiescent impoundment is included in CHEMDAT6. In addition, some general surface water computer models can be used to estimate emissions from naturally-aerated impoundments.

Occasionally a thin oil film will completely or partially cover the surface of an impoundment. Two methods of approximating emissions of volatile organics from the oil film are briefly discussed.

This section does not discuss emissions from disposal impoundments, for which no effluent flow occurs. An estimate of air emissions from a disposal impoundment can be made using the equations in Table 4-8 in Section 4.3.3.1 and a mass transfer coefficient calculated for a quiescent surface.

All the surface impoundment models included in this section assume that the two-film theory of mass transfer to the air is correct and that the concentration of hazardous chemicals above the impoundment is zero. If aeration is simulated, the models assume steady-state, completely-mixed conditions and further, that no non-aqueous liquids are present. The models of quiescent impoundments, which represent both steady- and non-steady-state conditions, are more diverse.

Many of the models described in this section were developed by the U.S. EPA (1987b). Thus, they use the same methods to determine volatilization, stripping, and biodegradation rates. These methods differ significantly from the work of Barton (1987) in developing NOCEPM:

1) The U.S. EPA (1987b) models do not consider adsorption, because it is assumed to be an insignificant removal mechanism. NOCEPM does model adsorption.

2) The U.S. EPA (1987b) diffused-aeration model assumes that the air bubbles in the subsurface are saturated with the compound of interest. Because equilibrium conditions are assumed, a stripping mass transfer coefficient need not be calculated. This assumption may or may not be valid, depending on the chemical. On the other hand, NOCEPM (Barton, 1987) includes a stripping equation which allows partial saturation of the air bubbles.

3) The U.S. EPA (1987b) models incorporate mechanical aeration by using different mass transfer correlations for volatilization from the turbulent surface area and the convective surface area. NOCEPM distinguishes between stripping from spray droplets caused by mechanical aeration and volatilization from the surface of the impoundment.

4) The U.S. EPA (1987b) models assume that the biodegradation rate is dependent on a constant biomass concentration and the substrate concentration. A weighting factor is also needed when multi-component wastes are simulated. In NOCEPM, the pseudo-first-order biodegradation rate is dependent on a constant biomass concentration and the concentration of the toxic organic.

Tables 4-9 and 4-10 summarize the characteristics and input requirements of the models in this section.

4.4.2 The Environmental Protection Agency Model for Quiescent Surface Impoundments

4.4.2.1 Summary--

Equations are presented in U.S. EPA (1987b) which can be used to estimate emissions of specific compounds from surface impoundments with quiescent surfaces. Only aqueous waste is considered and it is assumed that no separate organic phase exists. Both completely-mixed flow and plug-flow can be modeled (see Tables 4-11 and 4-12). Removal of organics from the system can occur with the effluent flow, through volatilization, and by means of biodegradation. Adsorption is not considered by the authors because research has shown that the chemicals most likely to volatilize tend to adsorb poorly. Likewise, other removal mechanisms are considered insignificant.

When the surface impoundment can be modeled as a steady-state completely mixed reactor, the concentration of a compound everywhere in the basin is equal to the effluent concentration of that compound. Because concentration is not a function of time, a simplified material balance can be written (Equation 1 in Table 4-11). For plug-flow, the concentration and the removal rates are a function of location and time, with the lowest concentration found in the effluent. In order to estimate the concentration of a compound in the effluent, the rate of compound disappearance (Equation 1 in Table 4-12) needs to be integrated over the hydraulic residence time (i.e., reactor volume divided by reactor flow rate). From the result, the fate of a compound can be predicted, but no information about peak removal rates is given.

For both types of flow, the volatilization rate is assumed to be the product of the concentration, the surface area and an overall mass transfer coefficient (see Equation 2 in Table 4-11). The two-resistance theory of mass transfer discussed in Section 2 is used to calculate the overall mass transfer coefficient value. The individual liquid-phase and gas-phase transfer coefficients needed to calculate the overall coefficient can be estimated using equations from Section 2. The authors use the Mackay and Matsugu equation (in Hwang, 1982) for gas-phase transfer and either the Mackay and

TABLE 4-9. SUMMARY MATRIX OF SURFACE IMPOUNDMENT MODEL CHARACTERISTICS

Characteristics	Model				
	EPA[1] & CHEMDAT6[1]	EPA[2] & CHEMDAT6[2]	EPA[3] & CHEMDAT6[3]	EPA[4] & CHEMDAT6[4]	NOCEPM
Aeration Method					
Surface aeration		X			X
Diffused aeration			X		X
None	X			X	
Time Domain					
Steady-state	X	X	X	X	X
Dynamic					
Spatial Domain					
1-dimensional	X	X	X	X	X
Flow					
Completely-mixed	X	X	X		X
Plug	X			X	
Degradation/ Transformation					
Volatilization	X	X	X	X	X
Stripping			X		X
Biodegradation	X	X	X		X
Sorption					X
Solution Technique					
Analytical					
--Hand calculation	X	X	X	X	
--Computer	X	X	X	X	X
Numerical					
Availability					
Published paper/report	X	X	X	X	
Proprietary					X
Public domain	X	X	X	X	

1 - Quiescent Surface
2 - Mechanically aerated system
3 - Diffused Air System
4 - Oil film on Quiescent Surface

TABLE 4-10. SUMMARY MATRIX OF SURFACE IMPOUNDMENT MODEL INPUT DATA

	Model								
Data Required	CHEMDAT6[1]	CHEMDAT6[2]	CHEMDAT6[3]	CHEMDAT6[4]	EPA[1]	EPA[2]	EPA[3]	EPA[4]	NOCEPM
Basin Characteristics									
Volume					X	X	X		X
Total surface area	X	X	X	X	X	X	X	X	X
Turbulent surface area		X				X	X		
Quiescent surface area		X				X	X		
Depth	X	X	X						
Oil film thickness				X					
Flow Rates									
Sparged gas			X				X		X
Total liquid	X	X	X		X	X	X		X
Oil film				X				X	
Concentration									
Compound influent:									
--in water	X	X	X		X	X	X		X
--in oil film				X				X	
Wasted cells									X
Active cells	X	X	X		X	X	X		X
Total organic carbon influent	X	X	X		X	X	X		
Effluent total suspended solids									X

1 - Quiescent surface
2 - Mechanically aerated system
3 - Diffused air system
4 - Oil film on quiescent surface

(continued)

TABLE 4-10. SUMMARY OF SURFACE IMPOUNDMENT MODEL INPUT DATA (concluded)

	Model								
Data Required	CHEMDAT6[1]	CHEMDAT6[2]	CHEMDAT6[3]	CHEMDAT6[4]	EPA[1]	EPA[2]	EPA[3]	EPA[4]	NOCEPM
Coefficients/ Constants									
Henry's Law							X		X
Octanol/water partition									X
Temperature	X	X	X	X			X		X
Volatilization constant:									
--turbulent area						X	X		
--quiescent area					X	X	X	X	
Biodegradation constant:									
--compound					X	X	X		X
--TOC	X	X	X		X	X	X		
Molecular weight									
--compound									X
--oil				X					
Surface reaeration rate									X
Diffusivity in water									
--compound									X
Density of oil				X					
Other									
Oil film residence time								X	
Total horsepower		X							X
Oxygen transfer efficiency		X							X
Wind velocity	X	X	X	X					X
Number of impellers		X							
Impeller diameter		X							
Impeller speed		X							
Power transfer efficiency		X							

1 - Quiescent surface
2 - Mechanically aerated system
3 - Diffused air system
4 - Oil film on quiescent surface

TABLE 4-11. IMPORTANT EQUATIONS IN THE EPA MODEL FOR A COMPLETELY-MIXED, QUIESCENT SURFACE IMPOUNDMENT

1) Material balance for a single-component system**

$$Q\ C_o = Q\ C_L + B\ b_i\ V\ C_L/C_o + K\ A\ C_L \tag{1}$$

where

Q = flow rate (m^3/s)
C_o = inlet concentration (g/m^3)
C_L = bulk liquid and effluent concentration (g/m^3)
B = biorate constant (g/s per g biomass)
b_i = biomass concentration (g/m^3)
V = volume (m^3)
K = overall mass transfer coefficient (m/s)
A = area (m^2)

2) Volatilization rate

$$E = K\ A\ C_L \tag{2}$$

where

E = air emissions from the liquid surface (g/s)

3) Biodegradation rate for a single-component system**

$$r = B\ b_i\ V\ C_L/C_o \tag{3}$$

where

r = biodegradation rate (g/s)

4) Weighting factor for one component of a multi-component system

$$W_1 = B_1\ C_{o1} \left[\sum_{i=1}^{n} B_i\ C_{oi} \right]^{-1} \tag{4}$$

where

W_1 = weighting factor for component 1 (dimensionless fraction)
B_1 = biorate for component 1 (g/s per g biomass)
C_{o1} = inlet concentration of component 1 (g/m^3)

TABLE 4-11. IMPORTANT EQUATIONS IN THE EPA MODEL FOR A COMPLETELY-MIXED, QUIESCENT SURFACE IMPOUNDMENT (concluded)

---

n - number of components in the mixture

B_i - biorate of component i (g/s per g biomass)

C_{oi} - inlet concentration of component i (g/m^3)

5) Effluent concentration**

$$C_L = Q\ C_o/(Q + B\ b_i\ V/C_o + K\ A) \qquad (5)$$

6) Fraction of compound volatilized

$$f_{air} = K\ A\ C_L/Q\ C_o \qquad (6)$$

where

f_{air} - fraction of volatilized compound

** When predicting the fate of one compound in a multi-component system, the biorate constant (B) in this equation should be replaced by the effective biorate constant (B * W), where W is a weighting factor calculated in equation 4.

TABLE 4-12. IMPORTANT EQUATIONS IN THE EPA MODEL FOR A PLUG-FLOW, QUIESCENT SURFACE IMPOUNDMENT

1) Rate of compound disappearance caused by biodegradation and volatilization for a single-component system**

$$-\frac{dC_t(V)}{dt} = B\ b_i\ V\ C_t/C_o + K\ A\ C_t \qquad (1)$$

where

C_t = concentration at time t (g/m^3)
t = time (s)
C_o = inlet concentration (g/m^3)
B = biorate constant (g/s per g biomass)
b_i = biomass concentration (g/m^3)
V = volume (m^3)
K = overall mass transfer coefficient (m/s)
A = area (m^2)

2) Equation (1) integrated from $C_t = C_o$ at $t = 0$ to $C_t = C_e$ at $t = V/Q$

$$C_e/C_o = \exp(-B\ b_i\ V/Q\ C_o - K\ A/Q) \qquad (2)$$

where

C_e = effluent concentration (g/m^3)
Q = flow rate (m^3/s)
C_e/C_o = fraction of compound leaving with the effluent

3) Fraction of the compound volatilized for a single-component system**

$$f_{air} = (1 - C_e/C_o)(K\ A)/(K\ A + B\ b_i\ V/C_o) \qquad (3)$$

where

f_{air} = volatilized fraction of the compound

4) Fraction of the compound biodegraded for a single-component system**

$$f_{bio} = (1 - C_e/C_o)(B\ b_i\ V/C_o)/(K\ A + B\ b_i\ V/C_o) \qquad (4)$$

where

f_{bio} = biodegraded fraction of the compound

TABLE 4-12. IMPORTANT EQUATIONS IN THE EPA MODEL FOR A PLUG-FLOW, QUIESCENT SURFACE IMPOUNDMENT (concluded)

5) Weighting factor for one component of a multi-component system

$$W_1 = B_1 C_{o1} \left[\sum_{i=1}^{n} B_i C_{oi} \right]^{-1} \qquad (5)$$

where

W_1 = weighting factor for component 1 (dimensionless fraction)

B_1 = biorate for component 1 (g/s per g biomass)

C_{o1} = inlet concentration of component 1 (g/m^3)

n = number of components in the mixture

B_i = biorate of component i (g/s per g biomass)

C_{oi} = inlet concentration of component i (g/m^3)

** When predicting the fate of one compound in a multi-component system, the biorate constant (B) in this equation should be replaced by the effective biorate constant (B*W), where W is a weighting factor calculated in Equation 5.

Yeun (1983) or the Springer et al. (1984) equation for liquid-phase transfer, depending on site-specific conditions. The authors state that for most volatile organics, the different equations developed to predict the individual transfer coefficients yield comparable results. The selection of equations can have some effect on results for semivolatiles because the mass transfer of less volatile organics is controlled by both liquid- and gas-phase resistance. Henry's law constant is incorporated into the gas-phase resistance term of the overall mass transfer coefficient. The model assumes that Henry's law constant has been estimated correctly and that its use is applicable (i.e., the waste is dilute), but Henry's constant is not important for volatile organics, for which mass transfer is liquid-phase controlled.

For both types of flow, the equation developed to estimate the rate of biodegradation (Equation 3 in Table 4-11) is pseudo-first-order with respect to concentration. It assumes one compound is the sole food source for the microorganisms, which are assumed to be suspended uniformly in the impoundment. According to the authors, in multicomponent systems, competition between the different organics will decrease the biodegradation rate of any specific compound. Therefore, the biorate constant for a single-component system B, should be multiplied by a weighting factor (Equation 4 in Table 4-11) to determine the effective biorate constant. The application of Equation 4 in Table 4-11 requires much more information than is normally available for any site. The authors simplify it in their example calculations by assuming the biorate constant for all the component compounds is the same. Then the equation reduces to the ratio of compound influent concentration to total influent concentration. The authors stress that their selected biodegradation model has not been validated. Because they have also found that the model results are very sensitive to the selection of biorate and biomass concentration values, they suggest the biodegradation term be set to zero for an environmentally conservative emission estimate.

4.4.2.2 Input Requirements--

For either type of flow, the input parameters which need to be supplied by the user are:

1) The flow rate (Q)

2) The volume of the impoundment (V)

3) The surface area (A)

4) The influent compound concentration (C_o)

5) The biorate constant for the compound (B)

6) The biomass concentration (b_i)

7) The overall mass transfer coefficient (K)

8) For multicomponent systems, the biorate constant and influent concentration of each component. When these can not be determined, the influent concentration of total organics is needed instead.

Values for most of these input parameters can be found readily. The most difficult parameters to estimate are the biomass concentration and the biorate constant. The authors provide a list of biorate constants for many chemicals. The user should note, however, that the values were obtained for zero-order kinetic conditions (i.e., when biodegradation rates are at a maximum and not influenced by changes in compound concentration, such as could be expected when a single-component waste is fed at high concentrations).

4.4.2.3 Output Description--

For completely-mixed continuous-flow conditions, the effluent concentration can be predicted using Equation 5 in Table 4-11. Once that value is known, the volatilization and biodegradation rates can be easily calculated. Equation 6 in Table 4-11 can also be used to determine the fraction of the compound volatilized.

For plug-flow conditions, Equation 2 in Table 4-12 can be used to determine the fraction of the compound which remains in the effluent flow. The fractions which have either volatilized or biodegraded are determined using Equations 3 and 4 in Table 4-12 respectively.

4.4.2.4 Resource Requirements--

The equations can be solved easily by hand and data is available in the literature to use this model for screening purposes.

4.4.2.5 Ease of Use--

The equations are straight forward. In addition, the authors discuss typical values for the input parameters and list some chemical-specific data. Therefore, it is an easy model to use.

4.4.2.6 Previous Applications--

The authors present example calculations. No applications to specific sites or comparisons with laboratory results have been found in the literature.

4.4.2.7 Availability/Documentation--

The model is described in U.S. EPA (1987b).

4.4.3 The Environmental Protection Agency Model for Mechanically-Aerated Impoundments

Mechanically-aerated impoundments are modeled in U.S. EPA (1987b) using the equations developed for quiescent surface impoundments in Section 4.4.2. The only significant difference between the two models is in the calculation of the overall mass transfer coefficient, K. The agitation of the mechanical aerator creates a turbulent surface area. Part of the total surface area may or may not be quiescent. Because mass transfer across turbulent surfaces differs from mass transfer across quiescent surfaces, the individual gas-phase and liquid-phase transfer coefficients are estimated using different correlations. The authors recommend the liquid-phase transfer coefficient equation of Thibodeaux (in Hwang, 1982) and the gas-phase transfer coefficient equation of Reinhardt (1977) for calculating the turbulent overall mass transfer coefficient. Both equations are discussed in Section 2. If part of the surface is quiescent, the quiescent overall mass transfer coefficient is calculated using the correlations recommended in Section 4.4.2.1.

The turbulent and quiescent coefficients need to be combined into a single coefficient for the whole system. This is done by weighting the two coefficients by the areas of each zone.

$$K = \frac{K_T\ A_T + K_Q\ A_Q}{(A_T + A_Q)} \tag{5}$$

where

K = system overall mass transfer coefficient (m/s)

K_T = turbulent overall mass transfer coefficient (m/s)

K_Q = quiescent overall mass transfer coefficient (m/s)

A = total surface area

A_T = turbulent surface area (m^2)

A_Q = quiescent surface area (m^2)

The overall mass transfer coefficient for the system, calculated from Equation 5 above, is used in the equations listed in Table 4-11.

All aspects of the model description in Section 4.4.2, other than the calculation of the mass transfer coefficient, are relevant to this model.

4.4.4 The Environmental Protection Agency Model for Diffused-Air Surface Impoundments

4.4.4.1 Summary--

Equations are presented in U.S. EPA (1987b) which can be used to estimate emissions from impoundments which are sparged with air. The equations are shown in Table 4-13. The development of the material balance in Equation 1 assumes that the impoundment is a completely-mixed, continuous flow system in steady-state. The material balance is almost identical to the material balance presented in Table 4-11 in Section 4.4.2 for a completely-mixed, quiescent impoundment. The difference is the addition of a fourth term on the right-hand side. That term accounts for the loss of a compound due to stripping. The three other terms account for removal from the system with the

TABLE 4-13. IMPORTANT EQUATIONS IN THE EPA MODEL FOR A COMPLETELY-MIXED, DIFFUSED-AIR SURFACE IMPOUNDMENT

1) Material balance for a single-component system**

$$Q\ C_o = K\ C_L\ A + Q_a\ K_{eq}\ C_L + B\ b_i\ V\ C_L/C_o + Q\ C_L \qquad (1)$$

where

Q_a = air flow rate (m^3/s)

K_{eq} = equilibrium constant

C_L = concentration in the liquid phase (g/m^3)

C_o = inlet concentration (g/m^3)

Q = flow rate (m^3/s)

B = biorate constant (g/s per g biomass)

b_i = biomass concentration (g/m^3)

V = volume (m^3)

K = overall mass transfer coefficient (m/s)

A = area (m^2)

2) Stripping rate

$$E_s = Q_a\ K_{eq}\ C_L \qquad (2)$$

where

E_s = stripping rate (g/s)

3) Equilibrium constant

$$K_{eq} = \frac{H}{RT} \qquad (3)$$

$$= 40.9\ H \text{ at } 25°C$$

where

H = Henry's Law constant ($atm\text{-}m^3/g\text{-}mol$)

R = Universal Gas constant ($8.21 * 10^{-5}$ $atm\text{-}m^3/g\text{-}mol\text{-}°K$)

T = temperature (°K)

TABLE 4-13. IMPORTANT EQUATIONS IN THE EPA MODEL FOR A COMPLETELY-MIXED, DIFFUSED-AIR SURFACE IMPOUNDMENT (concluded)

---

4) Volatilization rate

$$E_v = K\ A\ C_L \quad (4)$$

where

E_v = volatilization rate (g/s)

5) Biodegradation rate for a single-component system**

$$r = B\ b_i\ V\ C_L/C_o \quad (5)$$

where

r = biodegradation rate (g/s)

6) Effluent concentration**

$$C_L = \frac{Q\ C_o}{K\ A + Q_a\ K_{eq} + B\ b_i\ V/C_o + Q} \quad (6)$$

7) Weighting factor for one component of a multi-component system

$$W_1 = B_1\ C_{o1} \left[\sum_{i=1}^{n} B_i\ C_{oi} \right]^{-1} \quad (7)$$

where

W_1 = weighting factor for component 1 (dimensionless fraction)

B_1 = biorate for component 1 (g/s per g biomass)

C_{o1} = inlet concentration of component 1 (g/m^3)

n = number of components in the mixture

B_i = biorate of component i (g/s per g biomass)

C_{oi} = inlet concentration of component (g/m^3)

** When predicting the fate of one compound in a multi-component system, the biorate constant (B) in this equation should be replaced by the effective biorate constant (B*W), where W is a weighting factor calculated in Equation 7.

effluent flow, through natural volatilization, and through biodegradation. Other removal mechanisms, such as adsorption, are not considered significant and are omitted from the material balance.

The volatilization rate and biodegradation rate equations (Equations 4 and 5 in Table 4-13), have been discussed in Section 4.4.2. That discussion is not repeated here. One potential difference in determining the natural volatilization rate should be noted, however. The use of a diffused-aeration system may create a turbulent surface on the impoundment. If the surface is quiescent, the overall mass transfer coefficient can be calculated as discussed in Section 4.4.2. Otherwise, the authors recommend the use of the Thibodeaux (in Hwang, 1982) liquid-phase transfer coefficient and the Reinhardt (1977) gas-phase transfer coefficient equations (see Section 2) for calculating a turbulent overall mass transfer coefficient.

The stripping rate equation (Equation 2 in Table 4-13) is based on the simplifying assumption that the compound concentration in the air bubbles rising through the liquid is in equilibrium with the liquid-phase concentration. A stripping rate equation which allowed partial saturation of the bubbles would be more accurate. Such an equation was developed for the NCASI model, NOCEPM, in Section 4.1.5. The equilibrium constant in Equation 2 of Table 4-13 is the dimensionless form of the Henry's law constant. Henry's law constant, which is valid for dilute liquids, is assumed to be accurate for the waste being studied. The authors point out that certain waste mixtures in impoundments may deviate from Henry's law because of compound interactions or because the concentration is too high. They state, though, that errors applying Henry's law will tend not to underestimate the gas-phase concentration. Therefore, air emission estimates will tend to be conservative when Henry's law constant is inaccurate.

4.4.4.2 Input Requirements--

The input parameters needed to solve the equations in Table 4-13 are:

1) The flow rate (Q)

2) The volume of the impoundment (V)

3) The surface area (A)

4) The influent compound concentration (C_o)

5) The biorate constant for the compound (B)

6) The biomass concentration (b_i)

7) The overall mass transfer coefficient (K)

8) For multicomponent systems, the biorate constant and influent concentration of each component. When these can not be determined, the influent concentration of total organics is needed instead.

9) The air flow rate (Q_a)

10) Henry's law constant for the compound (K_{eq})

Values for most of these parameters are either known operating conditions for a site or can be estimated from the literature. The most difficult parameter to determine is the biorate constant. The authors provide biorate constants for a list of chemicals, but they should be used with caution. Model results are sensitive to the choice of the biorate constant and the constants provided were developed for different conditions than those found at most surface impoundments.

4.4.4.3 Output Description--

The effluent concentration can be calculated using Equation 6 in Table 4-13. Once that value is known the rates for stripping, volatilization, and biodegradation can be easily calculated.

4.4.4.4 Resource Requirements--

The equations can be solved easily by hand and data is available in the literature to use this model for screening purposes.

4.4.4.5 Ease of Use--

The equations are straight forward. In addition, the authors discuss typical values for the input parameters and list some chemical-specific data. Therefore, it is an easy model to use.

4.4.4.6 Previous Applications--

The authors present example calculations. No applications to specific sites or comparisons with laboratory results have been found in the literature.

4.4.4.7 Availability/Documented--

The model is described in U.S. EPA (1987b).

4.4.5 The EPA Spreadsheet CHEMDAT6

4.4.5.1 Summary--

Some of the analytical models developed in U.S. EPA (1987b) have been assembled into a Lotus 1-2-3 spreadsheet, called CHEMDAT6. CHEMDAT6 is included in U.S. EPA (1987b) as a floppy diskette for use on a personal computer and the CHEMDAT6 user's guide is incorporated into U.S. EPA (1987b) as an appendix.

Among the models available in CHEMDAT6 are the models described in Sections 4.4.2 through 4.4.4 for completely-mixed quiescent and aerated surface impoundments and in Section 4.4.9 for an oil film. In addition to modeling surface impoundments, CHEMDAT6 can be used to model activated sludge, sequencing batch reactor, and landfarming processes.

Using a Lotus 1-2-3 alternative command window, which provides menu driven instructions specific to CHEMDAT6, the user selects one or more compounds of interest from a data base and the type of simulation desired. Default input parameters supplied by CHEMDAT6 match the example calculations provided in U.S. EPA (1987b).

The CHEMDAT6 data base currently contains information on 61 chemicals or compounds. New chemicals can be added to the data base. To aid the user, the necessary information for approximately 700 chemicals is supplied in an appendix to U.S. EPA (1987b). The data base contains values for molecular weight, density, vapor pressure, Henry's law constant, diffusivity in water and air, boiling point, and zero-order biorates.

CHEMDAT6 is currently being revised. A help screen will be added to the new version to make the spreadsheet easier to use. In addition, more chemicals will be included in the data base. Most significantly, the biorate theory for surface impoundments and tanks is being revised. Monod kinetic constants will replace the zero-order biorates currently in the data base.

The CHEMDAT6 landfarming, activated sludge, and sequencing batch reactor models are discussed in Sections 4.1.6, 4.3.3.2, and 6.1.7, respectively. Information specific to the surface impoundment models is presented in the remainder of this section.

4.4.5.2 Input Requirements--

The input required by the four different surface impoundment model options in CHEMDAT6 are summarized in Table 4-14. Both diffused-air and mechanically-aerated systems are modeled by the CHEMDAT6 aerated impoundment model. A distinction is made between the two systems by setting unnecessary input parameters to zero. Quiescent surface impoundments are modeled by selecting the CHEMDAT6 non-aerated impoundment model. The CHEMDAT6 oil film model can also be used to simulate emissions from an oil film on the land. The two scenarios are distinguished by slightly different input requirements.

4.4.5.3 Output Description--

The CHEMDAT6 surface impoundment models calculate the fraction of a compound emitted to the air, biodegraded, and remaining in the effluent. Estimated annual emissions are also provided. The oil film model calculates the fraction of a compound emitted to the air. Output can be displayed on the screen or printed.

4.4.5.4 Resource Requirements--

Lotus 1-2-3 software and a personal computer are required to use CHEMDAT6.

TABLE 4-14. INPUT REQUIREMENTS FOR CHEMDAT6 SURFACE IMPOUNDMENT MODELS

Parameter	Nonaerated	Surface Aerated	Diffused Air	Oil Film
Windspeed	X	X	X	X
Depth	X	X	X	X
Area	X	X	X	X
Flow	X	X	X	X
Inlet compound concentration	X	X	X	
Total organic inlet concentration	X	X	X	
Total biorate	X	X	X	
Active biomass	X	X	X	
Temperature	X	X	X	X
Fraction of surface agitated		X		
Submerged air flow			X	
Number of impellers		X		
Oxygen transfer rate		X		
Total power		X		
Impeller diameter		X		
Impeller speed		X		
Power transfer efficiency		X		
Molecular weight of oil				X
Density of oil				X
Compound concentration in oil				X

4.4.5.5 Ease of Use--

The creators of CHEMDAT6 assume that the user has had some prior experience with Lotus 1-2-3. Instructions in the user's guide are minimal and a person unfamiliar with Lotus 1-2-3 spreadsheets is likely to be confused. The new version of CHEMDAT6 is expected to improve ease-of-use. The built-in data base is a useful feature.

4.4.5.6 Previous Applications--

The predictions of the non-aerated surface impoundment model in CHEMDAT6 have been compared to data from five quiescent impoundments. Agreement was within an order-of-magnitude, with the model both over or underpredicting the data. The validity of the aerated impoundment model has not been established.

4.4.5.7 Availability/Documentation--

CHEMDAT6 is available from the U.S. EPA, Office of Air Quality Planning and Standards, Research Triangle Park, N.C.

4.4.6 The NCASI Model (NOCEPM)

The National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI) has developed a screening model which predicts the intermedia distribution of organics in either an activated-sludge aeration tank or an aerated stabilization basin (ASB). The model, which is named the NCASI Organic Compound Elimination Pathway Model (NOCEPM), is described in detail in Section 4.1.5. The equations which form the basis of the model are identical for either application (see Table 4-7). Only the values of the input parameters will differ. The reader is referred to Section 4.1.5 for information on model assumptions, input, and output. Two points specific to ASB facilities are mentioned here.

One of the basic assumptions of the NOCEPM model is that the basin is completely mixed. ASB facilities are facultative, and thus, only partially-mixed. Nonetheless, because ASB's are primarily aerobic, the assumption of complete mixing is not a bad one (Barton, personal communication). In the future, the NCASI may expand the present model to account for partial mixing. They have already done this for an ASB model which estimates biological oxygen demand (BOD) removal (Barton and McKeown, 1986).

The model has been used to screen compounds in a hypothetical ASB wastewater. Comparison with a limited set of field data gave mixed results. It was concluded that more data are needed before the model can be evaluated for use with ASB facilities.

4.4.7 General Surface Water Computer Models

A number of computer models have been developed to estimate the fate of toxic chemicals in surface waters, such as rivers, lakes, and ponds. The codes which have been designed to model ponds can also be applied to large non-aerated surface impoundments. Two such general surface water models are introduced below. A third computer code which simulates a lagoon is also described. The models require more experience and more time to use than most of the models described in this report, but they are also more powerful. One important assumption made in all three models is that the chemical is present in low concentrations, as might be expected in a lake. The presence of surface oil or complex mixtures of chemicals may affect the validity of using these models. Most of the information provided in this section is based on summaries in Ambrose et al. (1988) and EPA (1987a).

4.4.7.1 The Exposure Analysis Modeling System (EXAMS-II)--

EXAMS-II (Burns, 1982 and 1985) was developed as a screening tool to estimate the long-term fate of organic chemicals at trace concentrations in fresh-water aquatic ecosystems. The one-, two-, or three-dimensional, finite-difference numerical model assumes either steady-state or monthly-varying conditions. Hydrologic transport and biochemical reactions, including photolysis, hydrolysis, biotransformation, oxidation reactions, sorption, and volatilization, are modeled for both a toxic chemical and its daughter products.

4.4.7.2 The Quality Simulation Program, Version 4 (WASP4)--

WASP4 (Ambrose et al., 1988) is a dynamic compartmental model. One aspect of the model is the simulation of the movement and fate of toxics in surface waters, including ponds, streams, lakes, rivers, and estuaries. The model supersedes two earlier models, WASTOX (Connolly and Winfield, 1984; Connolly and Thomann, 1985) and TOXIWASP (Ambrose et al., 1983) by incorporating components of each.

One component of the model, called TOXI4, simulates up to three interacting chemicals, present at low concentrations, and up to three sediment size fractions. The chemicals can be dissolved, sorbed on dissolved organic carbon, or sorbed to solids. Equilibrium is assumed. The transfer and transformation processes include sorption, volatilization, biodegradation, photolysis, hydrolysis, and ionization. First- and second-order kinetics are used.

4.4.7.3 The Environmental Protection Agency Lagoon Module--

A model of chemical release from waste disposal ponds has been developed for the U.S. EPA (Bicknell, 1984). The model has been formulated as a computer module for use in a linked multi-media analysis methodology. Water, sediment, and chemical mass balances are included. Volatilization, degradation, adsorption, diffusive exchange with the sediment, and transport with the effluent flow are considered. It is assumed that the lagoon, which is modeled as a number of layers, is completely-mixed and mechanically-aerated.

4.4.8 Other Surface Impoundment Models

Mills et al. (1985) develop a method to screen the fate and transport of toxic chemicals in non-aerated impoundments. Both steady- and non-steady-state conditions are discussed. The calculation of chemical concentration in the water phase is based on the assumption that the removal processes can be summed to give an overall first-order decay coefficient. Rate equations are presented for each of the removal processes: volatilization, biodegradation, hydrolysis, photolysis, and sorption on suspended solids. An example application of the toxicant screening method to a reservoir is included in the report.

Several models of volatilization from a surface impoundment are described in detail in Breton et al. (1984). Because volatilization is the only removal mechanism incorporated into these models, their use is not appropriate for bioremediation impoundments operating under normal conditions. One of the models, developed by Thibodeaux et al. (1982), simulates steady-state volatilization from both aerated and non-aerated impoundments. Aeration is accounted for by dividing the surface into turbulent and convective zones and calculating mass transfer coefficients for each zone. The two coefficients are weighted by area to obtain an overall mass transfer coefficient. (See Equation 5 in Section 4.4.3.)

4.4.9 The Environmental Protection Agency Model of Emissions from an Oil Film

The U.S. EPA (1987b) presents equations for estimating the emission of volatile organics from a thin oil film floating on the surface of an impoundment. Equations for both a well-mixed and plug-flow oil layer are shown in Table 4-15. The authors state that a well-mixed layer may result from changes in wind direction when the retention time is on the order of days, while the plug-flow equations apply when the oil film moves across the surface without backmixing.

A three-phase resistance approach should be used when calculating the overall mass transfer coefficient. Because it is difficult to determine the needed phase-specific transfer coefficients and the partitioning coefficients, the authors make a simplifying assumption that the gas-phase resistance controls mass transfer. Instead of Henry's law constant, Raoult's law is used to calculate the equilibrium coefficient and the Mackay and Matsugu correlation (in Section 2) is recommended to determine the gas-phase transfer coefficient. The product of the equilibrium coefficient and the gas-phase transfer coefficient equals the estimated overall mass transfer coefficient.

Biodegradation is neglected in this model, which only considers the pollutant in the oil film itself.

The research of Springer et al. (1985) suggests that equilibrium between the phases is not always realized and that oil-phase resistance is important in determining overall mass transfer. Therefore the assumptions in the U.S. EPA (1987b) model may not be appropriate. No example calculations or applications of the U.S. EPA (1987b) model are available.

4.4.10 The Springer et al. Model of Emissions from an Oil Film Under Windy Conditions

Springer et al. (1985) conducted laboratory investigations of the effect of oil films on the control of emissions. Their research has shown that oil

TABLE 4-15. IMPORTANT EQUATIONS IN THE EPA MODEL OF EMISSIONS FROM AN OIL FILM

For a Completely-Mixed Basin

1) Air emissions from the oil film

$$E = K\ A\ C_L \tag{1}$$

where

E = air emissions (g/s)
K = overall mass transfer coefficient (m/s)
A = surface area (m^2)
C_L = effluent compound concentration in the oil phase (g/m^3)

2) Effluent concentration in the oil phase

$$C_L = QC_o/(KA + Q) \tag{2}$$

where

Q = volumetric flow rate of the oil (m^3/s)
C_o = influent compound concentration in the oil phase (g/m^3)

For a Plug-Flow Basin

3) Fraction of the compound emitted to the air

$$f_{air} = 1 - \frac{C_e}{C_o} = 1 - \exp(-K\tau/D) \tag{3}$$

where

f_{air} = fraction of the compound emitted to the air
C_e = concentration in the effluent oil (g/m^3)
τ = residence time (s)
D = oil-film thickness (m)

4) The average emission rate

$$E_{ave} = f_{air}\ Q\ C_o \tag{4}$$

where

E_{ave} = the average emission rate (g/s) films cause significant reductions of volatile emissions from surface impoundments. As part of their research, the authors developed a chemodynamic model of emissions from a basin partly covered by an oil film. Such a partial covering can result from wind disturbance. Springer et al. state that when a basin is partially-covered, transfer occurs by parallel paths--from the water to the air and from the oil to the air--and that the oil is a competitive solvent for the volatile organic.

With the assumption that the air-phase concentration is negligibly small, the volatile organic emission rate, E, is given as:

$$E = K_w S_w C_w + K_o S_o C_o \tag{6}$$

where

K_w = the overall water phase mass transfer coefficient (m/s)

K_o = the overall oil phase mass transfer coefficient (m/s)

S_w = exposed surface area of the water phase (m^2)

S_o = exposed surface are of the oil phase (m^2)

C_w = water-phase concentration (kg/m^3)

C_o = oil-phase concentration (kg/m^3)

Based on previous experience, the authors assume that the water-phase overall mass transfer coefficient is liquid-phase controlled. However, the overall oil-phase mass transfer coefficient can be controlled by both the oil and gas phase. Thus, Springer et al. formulate a two-resistance equation.

$$\frac{1}{K_o} = \frac{1}{k_o} + \frac{1}{\theta\, k_g} \tag{7}$$

where

k_o = individual oil-phase coefficient (m/s)

k_g = individual gas-phase coefficient (m/s)

θ = equilibrium constant for the volatile between oil and air

The authors present a method of estimating k_o, if the individual water-phase coefficient, k_w, the diffusivities in oil and water, and kinematic viscosities in oil and water are known. The individual water-phase and gas-phase coefficients can be calculated by methods presented in Section 2. The equilibrium constant, θ, can be estimated as the compound's Henry's law constant divided by its oil/water partition coefficient. The water-phase concentration must be measured, but under equilibrium conditions, the oil-phase concentration can be approximated from the oil/water partition coefficient and the concentration in water.

Comparison of model predictions to laboratory results did not show consistent agreement. The authors concluded that: 1) the phases may not be in equilibrium in some cases, and 2) their method of calculating the individual oil-phase transfer coefficient may not be correct. The effect of wind on a non-aqueous liquid transfer coefficient is not understood thoroughly.

4.5 SENSITIVITY TO INPUT PARAMETERS

U.S. EPA (1987b) conducted analyses to evaluate the sensitivity of their surface impoundment models to variations in input parameter values. While the studies are specific to the EPA models for quiescent, mechanically-aerated, and disposal impoundments, the general findings are relevant to other models and other suspended-growth processes. Those results are summarized briefly.

Hydraulic detention time is an important parameter. The longer the detention time, the more semi-volatiles are emitted. When calculating long-term, averaged emissions, a standard temperature and wind speed were shown to be adequate. Wind speed does directly affect volatilization when it is a factor in estimating the mass transfer coefficient. Wind speed is not important for aerated basins. Temperature affects the value of Henry's law constant, which in turn is important in determining the magnitude of emissions of semi-volatile compounds. The emission of volatile compounds, for which mass transfer tends to be controlled by liquid-phase resistance, is not affected by the value of Henry's law constant (see Equation 11 in Section 2). The sensitivity analyses indicated that results are insensitive to diffusivity values. The models are very sensitive to all of the biodegradation parameters, however.

The important parameters related to mechanical aeration are the horsepower of the aerator and the size of the turbulent surface area. Variations in impeller diameter and speed, the oxygen transfer rate, and the oxygen correction factor affected results less. The U.S. EPA (1987b) diffused-air system model was not included in the study.

SECTION 5

MODELS OF FIXED-FILM SYSTEMS

5.1 INTRODUCTION

Four fixed-film bioremediation processes are described in Section 3.3. The use of these systems is not as widespread as the use of suspended-growth systems. In recent years they have been receiving more attention, particularly with regard to treating hazardous waste. However, the fixed-film systems are still less understood then suspended-growth systems, and thus, modeling and process design procedures are not as advanced. (Eckenfelder et al., 1989).

Most modeling efforts have concentrated on representing reactions within the biofilm of a fixed-film system. Early models considered the one-dimensional flux of a single limiting substrate, normally expressed as biological oxygen demand (BOD), through the film of attached microorganisms. Later, more complex biofilm models were developed to simulate the flux of an electron acceptor, such as oxygen through the biofilm and the secondary utilization of organics under both steady-state and non-steady-state conditions. Grady (1983) provides an excellent review of the development of biofilm models.

Biofilm models do not consider the geometry or the operational characteristics of specific systems. In the last ten years, some system-specific models have been developed. They were created to aid in system design and thus, model the removal of total substrate (e.g., BOD). None of the models address the issue of air emissions of volatile organics.

Air emissions are likely from both aerobic and anaerobic fixed-film systems. For aerobic systems, emissions will result from either passive volatilization at the liquid-air interface or stripping, if the systems are sparged with air. Gases, particularly methane, are produced during anaerobic bioremediation. Volatile organics present in anaerobic systems can partition into these gas bubbles as they rise through the system. Unless the gas is captured to be burned as an energy source, volatile organics can be emitted to the atmosphere.

Because air emissions are likely from fixed-film systems, perhaps on the same order-of-magnitude as from suspended-growth systems (McCarty, personal communication), and because no models exist to directly predict the magnitude of emissions, indirect methods of estimating emissions are needed.

For aerobic systems, Roberts et al. (1984) describe such an indirect method. They point out that there is an analogy between the transfer rates of volatile organics and the oxygen transfer rate. As was described in Section 2.2.3.5, a proportionality exists between the transfer rate constants of two compounds, which is independent of turbulence or the geometry of a system. The proportionality constant can be calculated from the liquid-phase diffusivities of the compounds. Oxygen is typically used as a reference compound.

$$\psi_i = \frac{k_{L,i}}{k_{L,O_2}} = \frac{K_{Li},a}{K_{LO_2},a} = \left(\frac{D_i}{D_{O_2}}\right)^n \qquad (1)$$

where

$k_{L,i}$ = liquid phase mass transfer ratio for component i (cm/s)

k_{L,O_2} = liquid phase mass transfer ratio for oxygen (cm/s)

$K_{L,i}a$ = overall transfer rate constant of component i (1/sec)

$K_{LO_2}a$ = overall mass transfer rate of oxygen in the liquid phase (1/sec)

D_i = diffusivity of compound i in water (cm^2/s)

D_{O_2} = diffusivity of oxygen in water (cm^2/s)

ψ_i = transfer rate constant proportionality coefficient

n = exponent between 0.5 and 1.0

The proportionality constant can be determined from literature values. If the overall mass transfer coefficient of oxygen is known, the overall mass transfer coefficient for a volatile organic compound can be estimated. Given the concentration of the compound in the system, the volatilization rate can be calculated.

Some of the models of fixed-film processes, particularly models of the rotating biological contactor (RBC) process, provide estimates of the overall oxygen transfer coefficient and the oxygen uptake rate. Those models, which may be of use in indirectly approximating emissions from fixed-film bioremediation processes, are briefly described in the following sections. They do not represent the entire literature on modeling fixed-film processes. The bibliography contains references to modeling efforts not discussed in this report.

Kissel (1986) lists values of measured or estimated oxygen mass transfer coefficients, taken from the literature, for the trickling filter and RBC processes. He points out that for these fixed-film systems, when calculating the overall mass transfer coefficient, $K_{LO_2}a$:

$$a = 1/\delta \qquad (2)$$

where

δ = the liquid-layer depth

a = the ratio of reactor surface area to liquid volume

Thus, an incorrect value for the liquid-layer depth, which is difficult to estimate, will lead to incorrect estimation of $K_{LO_2}a$. Kissel concludes that the mass transfer coefficients are subject to considerable uncertainty.

Clearly, the present generation of models of fixed-film processes are inadequate for the task of estimating the rate and magnitude of air emissions. More attention needs to be given to the issue, both in terms of theoretical modeling and in terms of collection of data from field and laboratory systems. Particularly, research is needed to determine the significance of air emissions from anaerobic processes.

5.2 TRICKLING-FILTER MODELS

Trickling filters are modeled as three-phase systems: a liquid film in contact with the biofilm at one interface and with the air on the other. They are characterized by extremely complex geometries and physical and biological processes (Muslu, 1984).

Design models for the trickling filter process often simulate laminar flow over an inclined flat plate. One such model is presented by Logan et al. (1987). Mass transfer of the substrate, BOD, and first-order biological removal are modeled. For granular-media trickling filters, Muslu (1984) presents a model of substrate removal efficiency based on dispersed flow and first-order biological removal of the substrate. Unfortunately, neither of these models considers mass transfer of oxygen.

For high organic loadings, when oxygen availability limits substrate utilization, methods proposed by Johnson and van Durme (1987) can be used to estimate the oxygen transfer rate, given information about BOD removal. The soluble BOD removal is converted to oxygen equivalent units using a factor of 0.57 mg O_2/mg soluble BOD removed. A temperature correction factor is applied if necessary. If the concentration of dissolved oxygen in the liquid can be measured or is known from operational experience, the mass transfer coefficient $K_{LO_2}a$, can then be approximated. This is because the transport rate is proportional to the difference between the saturation concentration and the dissolved concentration of oxygen, where the constant of proportionality is $K_{LO_2}a$.

If the overall oxygen transfer coefficient, $K_{LO_2}a$, can be estimated or if a value from the literature is used (see Kissel, 1986), the methods described in Section 5.1 can be used to estimate the volatilization rate of a priority pollutant. This will be an extremely rough approximation, however. Until more rigorous estimation methods are developed, it is more appropriate to rely on actual measurements of emissions.

5.3 ROTATING BIOLOGICAL CONTACTORS

The geometry and flow pattern in a rotating biological contactor (RBC) are simpler than in a trickling filter. RBC's can be operated either as continuous-flow or batch units. Factors which have a strong influence on the fate of organics during treatment in a RBC are the biofilm thickness, the rotational speed of the disks, and the organic loading (Atasi and Borchardt, 1984).

Volatilization of organics occurs across two types of air-liquid interfaces: the bulk liquid in the tank and the liquid film coating the rotating disks. Volatilization from the bulk liquid can be estimated using appropriate models described in Section 4. No RBC models directly estimate volatilization of specific compounds from the rotating disks. Several papers present equations for calculating the overall oxygen transfer coefficient, however. These can be used to estimate emissions.

Famularo et al. (1978) present a finite-difference model of simultaneous oxygen and substrate transport, with both liquid and biofilm resistances. The model assumes that the disks are 50% immersed, that the liquid on the disks does not move and is of constant thickness, that the tank is completely mixed, and that oxygen transfer in the tank is insignificant, because biological activity occurs on the disks only. Material balance equations are used to predict the concentration of the oxygen and the substrate in the effluent. The authors present the following equation for the oxygen mass transfer coefficient above the water line:

$$K_{LO_2} = \frac{D_{O_2}}{\delta/2} \qquad (3)$$

where

$$\delta = 25 + 6.85\ V^{2/3} \qquad (4)$$

and where

V = disk withdrawal velocity (cm/s)

δ = liquid film thickness in microns (μ)

Note that the value obtained from Equation 4 must be converted to appropriate units for use in Equation 3. As discussed in Section 5.1, the overall mass transfer coefficient, $K_{LO_2}a$ is calculated by multiplying the value from Equation 3 by the reciprocal of the liquid film thickness (see Equation 2).

The transfer rate from the gas phase to the film is given by:

$$\text{transfer rate} = K_{LO_2}/\delta\ (C^* - C^L) \qquad (5)$$

where

C^* = water concentration that would be in equilibrium with the actual air concentration

C^L = concentration in the film

By analogy, the volatilization rate of an organic pollutant from the disks would be:

$$\text{volatilization rate} = - \psi_i \, KL_i \, S^L/\delta \tag{6}$$

where

S^L = concentration of the compound in the film

Equation 6 assumes the concentration of the organic in the air is negligible and that the concentration of the organic in the film is known. That concentration value is affected by biological activity on the disk. A very conservative estimate can be made by assuming the concentration is equal to the concentration in the mixed tank.

Mueller et al. (1980) extend the work of Famularo et al. (1979) to include nitrification kinetics. The numerical model yields concentrations of both a carbonaceous and a nitrogenous substrate in the liquid film, the biofilm, and the tank. In addition to oxygen and substrate mass transfer, ammonia stripping and subsurface aeration are simulated by the model.

Suga and Boongorsrang (1984) develop a model of mass transfer in an RBC half immersed in water. They consider oxygen transfer onto the disks both above and below the water and present equations for estimating the average liquid film thickness on the disks and the oxygen transfer coefficient. The equations, which are much more complex than those of Famularo et al. (1978), are not presented here.

Vaidya and Pangarkar (1987) present a convective diffusion model for cases when the disks of an RBC are less than 50% submerged, which is commonly the case. The model, which considers variations in film thickness across the disk, predicts the transfer of solute gas. Calculations made by the authors using their model indicate that the oxygen mass transfer coefficient can be approximated as:

$$K_{LO_2} = (\omega)^{0.585} \tag{7}$$

where

ω = angular velocity (rad/sec)

Glaze et al. (1986) tracked the fate of naphthalene in a covered RBC. They used a value of K_{LO_2} equal to 5.0×10^{-6} m/s at 6 rpm in estimating the accumulation of naphthalene in the head space of the RBC. This value of K_{LO_2} is taken from the work of Bintanja et al. (1975), who measured values of K_{LO_2}

as a function of rotational velocity. Glaze et al. (1986) found that the predicted accumulation of naphthalene was over 1000 times the amount actually measured in the headspace. This is because their predictions did not consider the absorption into and the subsequent biodegradation in the biofilm of the chemical. Adsorption of the chemical onto the sludge was determined to be insignificant. Thus, their results indicate the possible conservatism of estimation methods which do not consider the biodegradation of a compound.

5.4 SUBMERGED PACKED BED MODELS

Submerged packed beds, both aerobic and anaerobic, have numerous applications, including treatment of soluble wastes, removal of ammonia, and nitrification (Hassan and Beg, 1987). They have become more popular in recent years because of their low space requirements, consistent performance, and relatively low cost.

Despite the increased attention given to submerged packed beds, few models of the process have been developed.

Lee and Stensel (1986) develop a steady-state model of substrate removal and oxygen utilization in a sparged reactor packed with a granular material. The model takes into account oxygen transfer to the biofilm both through bulk liquid dissolution and through direct contact between the gas bubbles and the biofilm. Comparison of their model simulations with laboratory results indicates that submerged packed beds can not be adequately modeled without including direct interfacial oxygen transfer. Among the equations presented by the authors is an expression for the oxygen dissolution rate from the air bubbles into the liquid for a small incremental section of the reactor. The equation assumes that each small section is completely mixed.

$$ODR_i = \int_z^{z+\Delta z} A\epsilon\alpha K_{LO_2}a(\beta C_s - C_L)dz \tag{8}$$

where

ODR_i = oxygen dissolution rate into the bulk liquid in the ith section of the reactor (g/h)

A = cross-sectional area of the packed bed reactor (m^2)

ϵ = void fraction of the packed bed reactor

α = wastewater-to-clean-water $K_{LO_2}a$ ratio

β = wastewater-to-clean water DO saturation value ratio

C_s = DO saturation concentration in clean water at the operating temperature and pressure (mg/L)

C_L = bulk liquid DO concentration (mg/L) z = distance from packed bed reactor bottom (m)

$K_{LO_2}a$ = the overall mass transfer coefficient for a sparged clean-water system (1/hr)

An analogous equation for the stripping of volatile organics can not be adapted from Equation 8, because the partial saturation of the air bubbles with the volatile organics is not accounted for.

An alternative way of estimating the stripping rate may be to assume that the concentration of any particular compound in the air bubbles is in equilibrium with the concentration of the liquid-phase concentration by the time it reaches the top of the reactor. If so, a stripping rate equation similar to that used by Namkung and Rittmann (1987) for an activated sludge unit can be used, without calculating a value for the overall mass transfer coefficient.

Hamoda and Abd-el-Bary (1987) investigate the characteristics of an aerated submerged fixed-film reactor. The reactor differs from the one modeled by Lee and Stensel (1986) in that compartments filled with vertical evenly-spaced, flat media plates are used to support the biofilm, rather than a granular medium. The authors found that the hydraulics of such a reactor can be described as a series of completely stirred-tank reactors, with each compartment completely-mixed.

Given the observation of Hamoda and Abd-el-Bary (1987) and ignoring biological reactions, the stripping rate in each compartment of this type of reactor can be estimated as for an activated-sludge unit. The effluent concentration of one compartment would be the influent concentration for the next.

Abramson (1987) develops a computer model of an anaerobic submerged packed bed treating domestic wastewater. The model predicts the effluent characteristics of both liquid and gas phases, based on influent wastewater characteristics. Mass balances for CH_4, CO_2, and N_2 are included in the model and are based on rates of biological and chemical production. The treatment of hazardous compounds is not considered by the author.

5.5 FLUIDIZED BED (EXPANDED BED) MODELS

A number of models have been developed to describe the fluidized bed processes. Some of the models assume a spherical, non-adsorbing support medium, such as sand, is used. Others consider the interaction of granular activated carbon (GAC) and a biofilm, both of which remove substrate. While some of the models are designed to simulate several complex components of the process, none of the models presents equations to describe mass transfer of oxygen to the bulk liquid, nor do they mention the emission of volatile organics. Thus, the models are only briefly summarized below.

Mulcahy et al. (1981) develop a model for a fluidized bed reactor, in which sand or some other non-adsorbing small particles support biofilm growth. The overall model links two components--a biofilm model of substrate utilization and a bed fluidization model which determines particle density and biofilm thickness. The overall model predicts substrate concentration as a function of axial position in the reactor.

Shieh et al. (1981) examine the factors affecting biomass concentration in an expanded bed reactor using experimental data and a model which predicts biomass concentration. They found that media size and biofilm concentration are important in determining biomass concentration.

Andrews and Trapasso (1984, 1985) present equations which describe adsorption and substrate utilization in a fluidized bed reactor using GAC. Factors considered include biofilm thickness, settling velocity of the GAC particles, and bed height. An equation is presented in the 1985 paper which predicts substrate removal for a specific bed height.

Most recently, Wang et al. (1986) develop and verify a biofilm model of substrate conversion in an expanded-bed, activated carbon anaerobic reactor.

SECTION 6

MODELS OF SOIL-INCORPORATION SYSTEMS

This section summarizes the current status of models which can be used to estimate the fate of organic pollutants during treatment in 3 types of soil-incorporation systems: land treatment, composting, and soil filter beds.

6.1 LAND TREATMENT (LANDFARMING) MODELS

6.1.1 Introduction

Both analytical and numerical models have been developed to describe the fate of a specific pollutant during the land treatment process. The good selection of models reflects the fact that landfarming is a widely used bioremediation process. Because oil refinery wastes account for more than half of all waste treated at landfarming facilities, many of the models are specifically designed to simulate an oily sludge incorporated into the soil. Models are available to simulate the fate of components of a dilute aqueous waste as well.

The steps involved in the land treatment process were described in Section 3.4.1. Air emissions can occur during each step. Since no one model considers all the steps, it may be necessary to apply two or more models to estimate the total emissions of a pollutant.

Volatilization can occur during waste application, the first step. Methods of estimating volatilization losses from either a spray or a waste stream issuing from a hose are presented in Section 6.1.2. In addition, Enfield et al. (1986) present a model for volatilization from a rapid-infiltration basin. If the waste is applied by means of subsurface injection, application is not modeled as a separate step because the waste is immediately incorporated into the soil.

Hours to days can pass between the time when the waste is applied and when it is tilled into the soil. Emission of volatile organics is likely to be significant during that time. If an oil film is visible on the surface of the waste, equations presented in Section 6.1.3 can be used to predict emissions. Otherwise, the authors of the RTI model (EPA, 1987b) state their model can be used. The biological decay term should be set to zero.

Most of the models start with the assumption that the waste has been incorporated into the soil to a specific depth. Within the soil, four mechanisms most strongly influence the fate of a pollutant: biodegradation, adsorption, vapor diffusion to the soil surface where volatilization occurs, and solute transport. Transport of dissolved chemicals to the surface by means of evaporation increases volatilization rates, while infiltrating water has the opposite effect. All four mechanisms are considered in the RITZ (Nofziger and Williams, 1988) and VIP (Stevens et al., 1989) computer models for oily waste and in the Jury et al. (1983) analytical model for dilute aqueous waste. The Jury et al. model has been modified to consider oily waste as well (Cadena et al., 1989). These models are described in Sections 6.1.4, 6.1.5, and 6.1.8. The analytical RTI model (EPA, 1987b) considers only vapor diffusion and biodegradation. The RTI model has been incorporated into the computer spreadsheet, CHEMDAT6. The compartmental screening method by Enfield et al. (1986) considers volatilization from a thin soil layer near the surface and transport in the lower soil column, but does not consider the mechanisms simultaneously.

Most of these models assume that the waste is surface-applied and uniformly-incorporated to a specific depth. Only one model, developed by Thibodeaux and Hwang (1982), can be used to simulate subsurface injection. Unfortunately, vapor diffusion, resulting in volatilization, is the only mechanism considered by the model. Thus, it will tend to overestimate emissions, except at very short times.

In general, air emissions from soil-incorporated waste are greatest immediately after tilling and decrease with time, as the distance vapors must diffuse to reach the soil surface increases. Retilling the soil redistributes the waste and can cause a temporary increase in emissions. The RTI model can be reapplied each time tilling occurs to simulate this effect.

The models discussed thus far can be used to estimate volatile emissions at land treatment facilities. However, emission of chemicals adsorbed to fugitive particulates can also occur during and after tilling, particularly under windy conditions and when the soil surface is dry. The estimation of contaminated particulate emissions is discussed in Section 6.1.10.

The models that are discussed in detail in this section consider the fate of only one component of the waste. They assume that:

1) Total air emissions from a waste can be calculated by summing the emission of each component, without considering interactions between the components.

2) The soil is homogeneous.

3) If liquid-phase transport is modeled, the flux is constant.

4) Vapor transport occurs only by diffusion.

All but the VIP model assume local equilibrium conditions exist. The Jury et al. and the RITZ models consider diffusion through a stagnant air layer at the soil surface, while the others assume the concentration of the chemical at the soil/atmosphere interface is zero. Model characteristics and input requirements are summarized in Table 6-1 and Table 6-2.

TABLE 6-1. SUMMARY MATRIX OF LAND TREATMENT MODEL CHARACTERISTICS

Characteristics	Model								
	Enfield et al.	EPA^1	EPA^2 & CHEMDAT6^2	EPA^3 & CHEMDAT6^3	Jury et al.	Modified Jury et al.	Parker & Jenkins	RITZ	VIP
Land Treatment Step									
Application	X	X					X		
Before incorporation			X	X					
After incorporation				X	X	X		X	X
Type of Waste									
Oily sludge		X	X	X		X		X	X
Dilute aqueous	X	X		X	X		X		
Processes Modeled									
Volatilization	X	X	X	X	X	X	X	X	X
Degradation									
--compound	X			X	X	X		X	X
--oil								X	X
Adsorption	X				X	X		X	X
Transport	X				X	X		X	X
Time Domain									
Steady-state		X							
Quasi-steady-state	X								
Dynamic			X	X	X	X	X	X	X
Spatial Domain									
1-dimensional	X	X	X	X	X	X	X	X	
Solution Technique									
Analytical									
--Hand calculation	X	X	X	X	X	X	X		
--Computer			X	X					
Numerical								X	X
Availability									
Published paper/report	X	X	X	X	X	X	X	X	
Proprietary									X
Public domain			X	X				X	

1 - Waste application model; 2 - Oil film model; 3 - Land treatment model

TABLE 6-2. SUMMARY MATRIX OF LAND TREATMENT MODEL INPUT DATA

Data Required	Model									
	CHEMDAT6^2	CHEMDAT6^3	EPA^1	EPA^2	EPA^3	Jury et al.	Modified Jury et al.	Parker & Jenkins	RITZ	VIP
Site Characteristics										
Surface area	X	X	X	X	X					
Depth of incorporation		X			X	X	X		X	X
Treatment zone depth									X	X
Oil film thickness	X			X						
Waste loading		X			X				X	X
Rates										
Evaporation						X	X		X	
Infiltration						X	X		X	X
Concentration										
Compound:										
--in water			X		X			X		
--in oil	X	X	X	X	X				X	X
--in soil						X	X			
Weight fraction of compound in oil					X				X	
Weight fraction of oil in the waste										X
Weight fraction of water in the waste										X
Volumetric fraction of waste in soil					X					

1 - Waste application model; 2 - Oil film model; 3 - Land treatment model

(continued)

TABLE 6-2. SUMMARY MATRIX OF LAND TREATMENT MODEL INPUT DATA (continued)

	Model									
Data Required	CHEMDAT6^2	CHEMDAT6^3	EPA^1	EPA^2	EPA^3	Jury et al.	Modified Jury et al.	Parker & Jenkins	RITZ	VIP
Coefficients/ Constants										
Temperature	X	X	X		X				X	X
Mass transfer coefficient:										
--compound gas phase			X	X	X			X		
--compound liquid phase			X					X		
--oxygen air/oil										X
--oxygen air/water										X
Degradation constant:										
--compound					X	X	X		X	X
--oil									X	X
Stoichiometric ratio of:										
--oxygen to compound consumed										X
--oxygen to oil degraded										X
Molecular weight										
--oil	X	X	X	X	X					
--air			X	X						
Diffusion coefficient:										
--in water						X	X			
--in air					X	X	X		X	
--of water in air									X	
Density:										
--oil	X		X	X					X	X
--air			X	X						
--soil bulk						X	X		X	X
Fraction organic carbon						X	X		X	
Compound partition coefficient:										
--organic carbon						X	X		X	
--soil/water										X
--oil/water									X	X
--Henry's law			X		X	X			X	X

1 - Waste application model; 2 - Oil film model; 3 - Land treatment model

(continued)

TABLE 6-2. SUMMARY MATRIX OF LAND TREATMENT MODEL INPUT DATA (concluded)

Data Required	Model									
	CHEMDAT6^2	CHEMDAT6^3	EPA^1	EPA^2	EPA^3	Jury et al.	Modified Jury et al.	Parker & Jenkins	RITZ	VIP
Coefficients/ Constants										
Oxygen partition coefficient:										
--air/oil										X
--air/water										X
Oxygen half-saturation constant:										
--air										X
--water										X
--oil										X
Volumetric content:										
--water						X	X			
--air		X			X	X	X			
--saturated		X			X				X	X
Pressure:										
--atmospheric			X	X						
--compound vapor			X	X	X					
Compound solubility in water							X			
Compound melting point							X			
Saturated hydraulic conductivity									X	X
Clapp and Hornberger constant									X	X
Other										
Residence time	X	X		X						
Oxygen transfer efficiency										
Wind velocity	X	X								
Radius:										
--droplet								X		
--waste stream			X							
Length of waste stream			X							
Relative humidity						X	X		X	

1 - Waste application model; 2 - Oil film model; 3 - Land treatment model

6.1.2 Models of Emissions during Waste Application

6.1.2.1 The Parker-Jenkins Model for Spray Application--

Parker and Jenkins (1986) present equations which can be used to estimate the loss of volatile organics during spray application of a dilute aqueous waste at a landfarming facility (See Table 6-3). Their method assumes that the rate of loss of a specific compound is proportional to its actual concentration in the spray. The concentration of the compound in the air is assumed to be zero. Two factors control the value of the rate loss coefficient, the radius of the spray droplets and the compound's overall transfer coefficient (see Equation 3). The overall transfer coefficient can be calculated using methods described in Section 2, and the droplet radius is found in the nozzle manufacturer's specifications. If the initial concentration of the compound and the droplet travel time are known, the loss of the compound can be easily calculated from Equation 2.

6.1.2.2 The Environmental Protection Agency Model for Waste Application--

The Environmental Protection Agency (1987b) presents methods of estimating volatile emissions from a waste stream issuing from a hose. The waste can be either an oily sludge or a dilute aqueous waste. The equations used to calculate emissions are listed in Table 6-4. Two assumptions made in developing Equation 1 are that the concentration of the compound in the waste stream is the same at all points in the stream and that the radius of the waste stream is constant. The first assumption will tend to overpredict emissions, but is not serious if the distance between the hose and the land surface is small. The Mackay and Matsugu and the Mackay and Yeun equations presented in Section 2 are recommended by the authors for calculating the gas-phase and liquid-phase transfer coefficients respectively. The authors have modified the gas-phase transfer coefficient equation, however, by multiplying its constant by two. They did this to account for the increase in mass transfer caused by the motion of the waste stream through the air. An example calculation is presented, but application of this method to a field site is not documented.

6.1.3 The Environmental Protection Agency Model of Emissions from an Oil Film

The Environmental Protection Agency (1987b) presents a method of predicting emissions from an unincorporated waste which has a visible oil film on top of it. The use of the equations, which are shown in Table 6-5, assumes that the oil film is very thin, that mass transfer is gas-phase controlled, and that the initial concentration in the waste is constant over the entire area. The authors suggest that the gas-phase transfer coefficient, k_g, be calculated using the Mackay and Matsugu equation presented in Section 2. Raoult's law is used to represent the equilibrium coefficient term, which is multiplied by the gas-phase transfer coefficient to determine the overall mass transfer coefficient. The only available application of this method is an example calculation.

TABLE 6-3. IMPORTANT EQUATIONS IN THE PARKER/JENKINS MODEL FOR SPRAY APPLICATION

1) Volatilization rate

$$\frac{dC_i}{dt} = - k_i C_i \qquad (1)$$

where

C_i = concentration of the volatile at a given time (M/L^3)
k_i = first-order rate coefficient ($1/T$)
t = time (T)

2) Result of integrating equation (1)

$$C_i = C_{i0} e^{-k_i t} \qquad (2)$$

where

C_{i0} = initial concentration (M/L^3)

3) Removal rate coefficient

$$k_i = \frac{K_{1i}}{r} \qquad (3)$$

where

K_{1i} = overall transfer coefficient (L/T)
r = droplet radius (L)

TABLE 6-4. IMPORTANT EQUATIONS IN THE EPA WASTE APPLICATION MODEL

1) Volatilization rate

$$E = K\ C\ A \qquad (1)$$

where

E = emission rate for the compound (g/s)
K = overall transfer coefficient (m/s)
C = compound concentration (g/cm^3)
A = surface area of the cylindrical waste stream (m^2)

2) Cylindrical area of the waste stream

$$A = 2\pi\ r\ \ell \qquad (2)$$

where

r = radius of the waste stream (m)
ℓ = length of the waste stream (m)

3) The overall transfer coefficient for the oily sludge

$$K = \frac{P^* \rho_a MW_{oil}}{P_o \rho_L MW_{air}} k_g \qquad (3)$$

where

P^* = compound vapor pressure (mm Hg)
P_o = atmospheric pressure (mm Hg)
ρ_a = density of air (g/cm^3)
ρ_L = density of oil (g/cm^3)
MW_{air} = molecular weight of air (g/g mol)
MW_{oil} = molecular weight of oil (g/g mol)
k_g = gas-phase transfer coefficient (m/s)

4) The overall transfer coefficient for the dilute aqueous waste

$$\frac{1}{K} = \frac{1}{k_L} + \frac{R\ T}{H\ k_g} \qquad (4)$$

TABLE 6-4. IMPORTANT EQUATIONS IN THE EPA WASTE APPLICATION MODEL (concluded)

where

k_L = liquid phase transfer coefficient (m/s)
H = Henry's Law constant (atm-cm^3/g-mol)
R = Universal Gas constant (atm-cm^3/g-mol-°K)
T = temperature (°K)

TABLE 6-5. IMPORTANT EQUATIONS IN THE EPA MODEL OF EMISSIONS FROM AN OIL FILM

1) Emission rate for a compound

$$E = K\ C_t\ A \qquad (1)$$

where

E = emission rate for constituent (g/s)
K = overall mass transfer coefficient (m/s)
C_t = concentration of constituent in the oil phase at time t
A = area of land treatment (m^2)

2) Concentration of the compound in the oil at time t

$$C_t = C_o\ [\exp(-Kt/D)] \qquad (2)$$

where

C_o = initial concentration of constituent in the waste
D = oil film thickness (m)
t = time (s)

3) Overall mass transfer coefficient

$$K = \frac{P^* \rho_a\ MW_{oil}}{P_o \rho_L\ MW_{air}}\ k_g \qquad (3)$$

where

P^* = compound vapor pressure (mm Hg)
P_o = atmospheric pressure (mm Hg)
ρ_a = density of air (g/cm^3)
ρ_L = density of oil (g/cm^3)
MW_{air} = molecular weight of air (g/g mol)
MW_{oil} = molecular weight of oil (g/g mol)
k_g = gas-phase transfer coefficient (m/s)

6.1.4 The Regulatory and Investigative Treatment Zone Model (RITZ)

6.1.4.1 Summary--

Nofziger and Williams (1988) present an interactive one-dimensional computer model, called RITZ, which predicts the transport and fate of hazardous chemicals after a single application of an oily sludge to a land treatment facility. The mathematical equations incorporated into RITZ were developed by Short (1985). Some of the more important equations are shown in Table 6-6.

RITZ assumes the treatment zone is divided into two sections (see Figure 3-12 in Section 3). The first zone is the plow zone--the depth to which the sludge is incorporated into the soil by tilling. The lower zone is treated as a semi-infinite column. Thus, no contaminant leaves the lower zone. The processes considered in the model are the downward transport of the chemical in the liquid phase, volatilization, lumped biological and chemical degradation, and adsorption. The effect of oil in the sludge in retarding transport is also incorporated into the model, which means that the model is not applicable to the landfarming of non-oily wastes.

The simplifying assumptions made in developing the model are listed below.

1) The waste is instantaneously and uniformly mixed into the plow zone. Research has shown that many volatile organics are lost to the atmosphere prior to tilling in the landfarming process. Because the model estimates emissions only after tilling has occurred, it will underestimate total emissions.

2) The oily sludge does not migrate. Thus, it is never present in the lower treatment zone.

3) The four phases in the system are in local equilibrium. The partitioning between the aqueous and all other phases is described by linear isotherms.

4) Both the pollutant and the oil degrade with time. Degradation kinetics are first-order. The rate constants do not change with time or depth. Thus, they ignore changes in biological activity with depth and the influence of the loading rate.

5) The water flux is constant.

6) Dispersion is ignored, resulting in plug flow. Actual dispersion in the field will cause the pollutant to arrive at a specific depth sooner and stay longer than predicted by the model. In the model, a pollutant slug moves downward with time. The total concentration above and below the slug is zero at all times.

7) The soil characteristics are uniform. This assumption is also not met under field conditions.

TABLE 6-6. IMPORTANT EQUATIONS IN THE REGULATORY AND INVESTIGATIVE TREATMENT ZONE MODEL (RITZ)

1) The total concentration in the pollutant slug at position x and time t

a) top of pollutant slug $\leq$ x $\leq$ pzd

$$C_T(x,t) = C_{To} \exp(-\mu_p t) \tag{1}$$

b) pzd < x $\leq$ bottom of pollutant slug

$$C_T(x,t) = C_{To} R \exp(-\mu_p t)/(R + R_T \exp(-\mu_o(t-(x-pzd)/V_p))) \tag{2}$$

where

C_{To} = initial pollutant concentration (g/m^3)

μ_p = degradation constant for the pollutant (1/day)

= $\ln(2)/t_{\frac{1}{2}p}$

$t_{\frac{1}{2}p}$ = half-life of pollutant (day)

μ_o = degradation constant for the oil (1/day)

= $\ln(2)/t_{\frac{1}{2}o}$

$t_{\frac{1}{2}o}$ = half-life of oil (day)

R = retardation factor for the pollutant in the treatment zone

R_T = contribution of oil to the retardation

V_p = velocity of the pollutant in the lower treatment zone (m/day)

pzd = depth of the plow zone (m)

2) The initial total pollutant concentration

$$C_{To} = SAR \cdot S_p / (10^4 \; pzd) \tag{3}$$

where

SAR = sludge application rate (kg/ha)

S_p = concentration of pollutant in the sludge (g/kg)

3) The retardation factor ignoring oil

$$R = 1 + (\rho K_D + (\theta_s - \theta)K_H) / \theta \tag{4}$$

TABLE 6-6. IMPORTANT EQUATIONS IN THE REGULATORY AND INVESTIGATIVE TREATMENT ZONE MODEL (RITZ) (continued)

where

ρ = bulk density of the soil (kg/m^3)
θ = water content of the soil on a volume basis (m^3/m^3)
θ_s = saturated water content of the soil on a volume basis (m^3/m^3)
K_D = partition coefficient for pollutant in the soil (m^3/kg)
K_H = dimensionless value of Henry's Law constant

4) Retardation of pollutant because of oil

$$R_T = \phi_o(K_o - K_H) / \theta \tag{5}$$

where

ϕ_o = initial oil content or the volume fraction occupied by oil (m^3/m^3)
K_o = partition coefficient for oil

5) Velocity of pollutant in the lower treatment zone

$$V_p = \frac{V_d}{\theta R} = \frac{V_a}{R} \tag{6}$$

where

V_d = recharge rate (m/day)
V_a = pore water velocity (m/day)

6) The concentration of the pollutant in water in the pollutant slug at position x and time t

a) top of pollutant slug $\leq x \leq$ pzd

$$C_W(x,t) = C_T(x,t) / (\theta(R + R_T \exp(-\mu_o t))) \tag{7}$$

b) pzd $< x \leq$ bottom of pollutant slug

$$C_W(x,t) = C_T(x,t) / (R\theta) \tag{8}$$

TABLE 6-6. IMPORTANT EQUATIONS IN THE REGULATORY AND INVESTIGATIVE TREATMENT ZONE MODEL (RITZ) (continued)

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where

C_W = pollutant concentration in water (g/m^3)

7) Volume fraction of oil in the plow zone at time t

$$\phi(t) = \phi_o \exp(-\mu_o t) \tag{9}$$

8) Initial volume fraction of oil

$$\phi_o = \mathrm{SAR} \cdot S_o / (10^7 \rho_o \, \mathrm{pzd}) \tag{10}$$

where

S_o = concentration of oil in the sludge (g/kg)

ρ_o = density of oil (kg/m^3)

9) Time when the top of the pollutant slug reaches a specified depth

a) $0 \le x_{top} \le \mathrm{pzd}$

$$t_{top}(x_{top}) = \mu_o^{-1} \ln\{(1 + R_T/R) \exp[\mu_o \, x_{top}/V_p - F(x_{top})] - R_T/R\} \tag{11}$$

b) $\mathrm{pzd} < x_{top} \le \mathrm{tzd}$

$$t_{top}(x_{top}) = t_{top}(\mathrm{pzd}) + (x_{top} - \mathrm{pzd})/V_p - G(x_{top}) \tag{12}$$

where

$F(x_{top}) = \mu_o \, a \, V_p^{-1} \ln(1 + x_{top}/g)$

$G(x_{top}) = a \, V_p^{-1} \ln[(g + x_{top})/(g + \mathrm{pzd})]$

$g = D_S \, \delta / D_A + a$

$a = K_H \, D_S / (V_a \theta)$

D_A = diffusion coefficient of the pollutant vapor in air (m^2/day)

D_S = diffusion coefficient of the pollutant vapor in the soil (m^2/day)

δ = thickness of the stagnant boundary layer above the soil (m)

x_{top} = location of the top of the slug (m)

t_{top} = time when top of slug reaches position x_{top} (day)

tzd = depth of the treatment zone (m)

TABLE 6-6. IMPORTANT EQUATIONS IN THE REGULATORY AND INVESTIGATIVE TREATMENT ZONE MODEL (RITZ) (concluded)

10) Flux of the pollutant vapor for a specified position of the top of the pollutant slug at the corresponding time

a) $0 \le x_{top} \le pzd$

$$J(t) = a\ V_p\ C_{To}\ \exp(-\mu_p t)/\{(g - a + x_{top})[1+(R_T/R)\exp(-\mu_o t)]\} \qquad (13)$$

b) $pzd < x_{top} \le tzd$

$$J(t) = a\ V_p\ C_{To}\ \exp(-\mu_p t)/\{(g - a + x_{top})[1+(R_T/R)\exp(-\mu_o \Delta t)]\} \qquad (14)$$

where

$t = t_{top}\ (x_{top})$

$\Delta t = t_{top}(x_{top}) - (x_{top} - pzd)/V_p$

8) Volatilization is controlled by diffusion through the soil above the slug and diffusion through a stagnant boundary layer above the soil. The stagnant boundary layer is modeled after the work of Jury et al. (1983) and is described in Section 6.1.8.

9) The Clapp and Hornberger (1978) relationship is used to calculate the water content of the soil, based on the soil's hydraulic conductivity.

Because of these simplifying assumptions, RITZ is best used as a screening model for use in studying specific hazardous chemicals associated with the landfarming process. The authors suggest that an expected range of parameter values be used to obtain a measure of uncertainty in the results.

6.1.4.2 Input Requirements--

The input parameters which must be specified are:

1) Fraction organic carbon in the soil
2) Bulk soil density and the density of the oil
3) Saturated water content
4) Saturated hydraulic conductivity
5) Clapp and Hornberger constant
6) Concentration of the pollutant and of oil in the sludge
7) Organic carbon partition constant
8) Oil-water partition coefficient
9) Henry's law constant
10) Diffusion coefficient of the pollutant and of water vapor in air
11) Half-lives of the pollutant and the oil
12) Sludge application rate
13) Plow zone and treatment zone depths
14) Recharge and evaporation rates
15) Air temperature
16) Relative humidity

Initially, data are entered manually using a data entry editor, which uses a screen format. Data within each screen can be modified in any sequence. The completed data set can be saved to a file for future use. At the end of data entry, the parameters are automatically checked for consistency. In addition, some help is provided in estimating unknown parameters.

6.1.4.3 Output Description--

The data entry editor is used to specify the tabular and graphical output desired for each run. Graphical output options include line graphs of concentration as a function of time or depth, of slug location as a function of time, and of the amount volatilized or leached as a function of time. Bar graphs show the concentrations in different phases, and a pie graph shows the mass balance distribution. The same information, as well as a list of the input and calculated parameters, can be displayed in tabular form.

6.1.4.4 Resource Requirements--

According to Nofziger and Williams (1988), the computer model is designed for use on a personal computer (PC) with at least 256 Kbytes of random access memory. A 8087 or 80287 math coprocessor and PC-DOS or MS-DOS are required. Tabular output can be generated on a monochrome PC. A color/graphics board and monitor are needed for graphical displays.

6.1.4.5 Ease of Use--

The interactive design of RITZ makes it a very easy model to use. Runs are completed within seconds and repeated runs can be made by modifying one or more parameters each time. The addition of an on-line data base would make the model even easier to use. If the model is used for screening purposes, the input data can be estimated from the literature.

6.1.4.6 Previous Applications--

Field verification of the model is in progress, but results are not available at this time. An example problem is presented in the user's guide.

6.1.4.7 Availability/Documentation--

RITZ was developed for and by the U.S. EPA. It is available by contacting the U.S. Environmental Protection Agency, R.S. Kerr Laboratory, Groundwater Research Branch, P.O. Box 1198, Ada, Oklahoma 74820. It is documented in Nofziger and Williams (1988).

6.1.5 The Vadose Zone Interactive Processes Model (VIP, Version 3.0)

6.1.5.1 Summary--

The Vadose Zone Interactive Processes Model (VIP, Version 3.0), developed at Utah State University, predicts the fate of hazardous compounds in the unsaturated zone after application and incorporation at a land treatment facility. Version 2.0 of the computer model is described in Grenney et al.

(1987) and Symons et al. (1988). Version 3.0 is described in Stevens et al. (1989). The main difference between Version 2.0 and 3.0 is that the new version considers the effect of oxygen availability on biodegradation. The model is designed for use on an IBM personal computer or a compatible computer. Input data files can be constructed using either a built-in editor, LOTUS spreadsheet files, or a word processor. Runs can be made in either single- or multiple-run format. When a single run is made, on-screen graphics are available to summarize results.

The fate of either a specific pure compound or a mixture, which exhibits homogeneous chemical properties and can be treated as a compound, is predicted by the VIP model for each of four phases: water, oil, soil, and pore air. The factors influencing the fate of the compound are volatilization, degradation (which can be oxygen-limited), adsorption/desorption, advection, and dispersion. Grenney et al. (1987) explain that the VIP model has extended the work of Short (1986) to include site-specific information about application rate and frequency, temperature, degradation, soil-water partition coefficients as a function of depth, and non-zero initial concentrations in the soil.

The important equations in Version 2.0 of the VIP model are listed in Grenney (1987). These equations, modified to reflect information in the Version 3.0 Users Manual (Stevens et al. 1989), are listed in Table 6-7. The equations which describe the oxygen concentration in each phase are not shown. The equations are solved numerically, using a modular structure. The modular structure allows more than one numerical solution technique to be used in the model.

Symons et al. (1988) list the model assumptions. They are:

1) The soil is homogeneous, with constant porosity, bulk density, and chemical properties. A soil column with unit cross-sectional area is considered.

2) The waste is a mixture of oil, water, specific compounds, and inert matter. The physical and chemical characteristics of the waste remain constant during an application period.

3) The waste is applied instantaneously and uniformly to a zone of incorporation of user-specific depth. (At landfarming sites, the zone of incorporation is approximately 15 cm deep and the depth of the total treatment zone is approximately 1.5 meters).

4) Waste application occurs periodically at specified intervals.

5) Four phases exist in the soil column: water, oil, soil, and air. The oil phase can not move below the zone of incorporation.

6) The monthly soil water content is estimated from soil properties using the Clapp and Hornberger (1978) procedure.

TABLE 6-7. IMPORTANT EQUATIONS IN THE VIP MODEL

1) The rate of change in compound concentration in the aqueous phase

$$\begin{aligned}\frac{\partial C_w}{\partial t} = &- V_w \frac{\partial C_w}{\partial z} - \mu_w C_w \left[\frac{O_w}{K_w + O_w}\right] \\ &- \frac{\kappa}{\theta_w} (\theta_a K_{aw} + \theta_o K_{ow} + \rho K_{sw}) C_w \\ &+ \frac{\kappa}{\theta_w} (\theta_a C_a + \theta_o C_o + \rho C_s) \qquad (1)\end{aligned}$$

where

C_w = concentration in the water phase (g/m^3)
V_w = vertical pore velocity of water (m/day)
μ_w = compound's first-order decay rate in water (1/day)
κ = mass transfer rate coefficient (1/day)
θ_w = water volume within the control volume (m^3 water/m^3 total)
θ_a = air volumetric content (m^3 air/m^3 total)
θ_o = oil volumetric content (m^3 oil/m^3 total)
ρ = soil bulk density (g soil/m^3 total volume)
K_{aw} = linear air-water partition coefficient (g/m^3 air per g/m^3 water)
K_{ow} = linear oil-water partition coefficient (g/m^3 oil per g/m^3 water)
K_{sw} = linear soil-water partition coefficient (g/m^3 soil per g/m^3 water)
t = time (days)
z = depth (m)
O_w = oxygen concentration in water (g/m^3)
K_w = oxygen half saturation constant in water (g/m^3)
C_a = compound concentration in the air phase (g/m^3)
C_o = compound concentration in the oil phase (g/m^3)
C_s = compound concentration in the solid phase (g/m^3)

TABLE 6-7. IMPORTANT EQUATIONS IN THE VIP MODEL (continued)

2) The rate of change in compound concentration in the air phase

$$\frac{\partial C_a}{\partial t} = - V_a \frac{\partial C_a}{\partial z} + D_a \frac{\partial^2 C_a}{\partial z^2} - \mu_a C_a \left[\frac{O_a}{K_a + O_a}\right] \qquad (2)$$

where

V_a = vertical pore velocity of air (m/day)
D_a = dispersion coefficient for air (m^2/day)
μ_a = compound's first-order decay rate in air (1/day)
O_a = oxygen concentration in air (g/m^3)
K_a = oxygen half saturation constant in air (g/m^3)

3) The rate of change in compound concentration in the oil phase

$$\frac{\partial C_o}{\partial t} = - \mu_o C_o \left[\frac{O_o}{K_o + O_o}\right] + \kappa (K_{ow} C_w - C_o) - C_o \frac{\partial \theta_o}{\partial t} \qquad (3)$$

where

μ_o = compound's first-order decay rate in oil (1/day)
O_o = oxygen concentration in oil (g/m^3)
K_o = oxygen half saturation constant in oil (g/m^3)

4) The rate of change in compound concentration in the soil-grain phase

$$\frac{\partial C_s}{\partial t} = - \mu_s C_s + \kappa (K_{sw} C_w - C_s) \qquad (4)$$

where

μ_s = compound's first-order decay rate on soil grains (1/day)

5) The rate of change in volumetric content for the oil

$$\frac{\partial \theta_o}{\partial t} = - \gamma_o \theta_o \left[\frac{O_o}{K\gamma + O_o}\right] \qquad (5)$$

TABLE 6-7. IMPORTANT EQUATIONS IN THE VIP MODEL (concluded)

where

γ_o = degradation rate of the oil (1/day)

$K\gamma$ = oxygen half saturation constant with respect to oil decay (g/m^3)

6) The volumetric content of air

$$\theta_a = \phi - \theta_w - \theta_o \qquad (6)$$

where

ϕ = soil porosity

7) The recharge rate and temperature at the site remain constant during any month or season.

8) Abiotic decay mechanisms are insignificant. Thus, biodegradation is the only decay mechanism considered.

9) Biodegradation is affected by both a first-order decay rate and the oxygen concentration and half saturation constant in each phase. Separate decay coefficients, which can vary with depth, need to be identified for each phase.

10) Pore velocity, diffusion, and dispersion are constant with depth. Dispersion in the water phase is not modeled.

11) Mass transfer occurs between water and each of the other phases.

12) Adsorption/desorption between water and each of the other phases is described as a linear-gradient process. Non-equilibrium adsorption/desorption kinetics are modeled. (However, local equilibrium can be simulated by using a large rate constant).

13) Volatilization occurs because of mass flux into the air phase from water and then advection/dispersion in the air phase.

14) The concentration of the compound in the air is zero.

6.1.5.2 Input Requirements--

1) Soil property input data include porosity, bulk density, the Clapp and Hornberger (1978) moisture coefficient, monthly saturated hydraulic conductivity and initial compound concentration in the air, water and soil phases.

2) Input data related to site operation include the plow zone and treatment zone depths, and the waste application rate, period, and frequency.

3) Waste and environmental properties input data include the weight fraction of oil and of water in the waste, the density of the soil and waste, the compound concentration, the site temperature for each zone for each month, the mean daily recharge rate for each month, and a temperature correction coefficient for each month.

4) Input data related to the modeled fate mechanisms include a compound partitioning coefficient for each zone between water and oil, between water and soil and between water and air (for a total of 6), a compound adsorption/desorption rate coefficient between water and oil, air, and soil (total of 3), a compound biodegradation rate constant for each zone and each phase (total of 8), the oil decay rate, oxygen partition coefficients for each zone between air and oil and air and water (total of 4), oxygen half saturation constants within the air, oil, and water phases for each zone (total of 6), an

oxygen transfer rate coefficient between air and oil and air and water (total of 2), and the stoichiometric ratio of oxygen to compound consumed and of oxygen to oil consumed.

Many of these site- and waste-specific input parameters will need to be determined by data collection in the field and laboratory and/or by careful selection of published values. The researchers at Utah State University have compiled a data base of some of the input parameters, including partition coefficients and biodegradation rates, for many chemicals of interest. The current data base represents data published through 1988. It is provided free-of-charge to the Environmental Protection Agency and available for purchase by others.

Data for the oxygen half saturation constants are not available in the literature. The authors of Version 3.0 suggest that when a user does not have information for this parameter, a small value be used (which means that oxygen is not limiting biodegradation).

6.1.5.3 Output Description--

VIP contains a number of output options which are selected by the user at the beginning of each run. The options include writing to files:

1) the input data to an echo file

2) an initial condition profile

3) the depth profile of compound concentration at different times

4) the summary depth profile of concentration in each phase

5) mass balance summary information over time

In addition, the final summary output can be displayed on-screen in graphical form.

6.1.5.4 Resource Requirements--

The VIP model (Version 3.0) is programmed for use on an IBM PS/2 or PC compatible computer with CGA display adapter and monitor and an Epson or IBM compatible graphics printer. As stated above, creation of an input data file will require the use of field and laboratory data or the careful use of literature values.

6.1.5.5 Ease of Use--

Once accurate input data have been identified, the model's interactive format, built-in editor, and on-screen graphics capability make VIP easy to use. In addition, Grenney et al. (1987) state that the model can easily be modified and upgraded because of its modular structure. The difficulty for some users may be in building a site-specific input data set. The model is not intended for use as a screening tool.

6.1.5.6 Previous Applications--

No applications of Version 3.0 of the model are published at this time. Grenney et al. (1987) state that Version 2.0 agreed well with laboratory results for three polynuclear aromatic hydrocarbons (PAH). Symons et al. (1988) report that Version 2.0 underpredicted laboratory results for concentrations in the incorporation zone, but was able to predict the depth of migration for seven PAH. They found that predicted results were most sensitive to the choice of degradation rate and initial soil concentration. The VIP model is currently being field tested by the Environmental Protection Agency.

6.1.5.7 Availability/Documentation--

This proprietary model and the data base described above are available free-of-charge to the Environmental Protection Agency. Others can purchase either or both by contacting: Dr. D. Stevens, Department of Civil and Environmental Engineering, Utah State University, Logan, Utah, 84322-4110.

6.1.6 The Environmental Protection Agency Land Treatment Model (RTI Model)

6.1.6.1 Summary--

A model developed by Clark Allen at the Research Triangle Institute, called the RTI model, is described and recommended in U.S. EPA (1987b) for use in estimating emissions from land treatment facilities. Emissions from either oily sludge or dilute aqueous waste, which has been uniformly tilled into the soil to a specified depth, can be predicted. In addition, the effects of each subsequent retilling of the soil and reapplication of waste can be modeled. The waste is assumed not to advect or diffuse out of the zone of incorporation.

Based on Fick's second law of diffusion for a flat slab, two emission rate equations, one short-term and one long-term, are presented (Equations 1 and 2 in Table 6-8). The equations are based on the assumption that the gas is immobile. In all but the first hours after application or tilling, emissions from the surface are controlled by diffusion of vapors through the soil pores. In the short-term, when emissions are greatest, the rate is controlled by gas-phase mass transfer at the soil surface. After the volatiles at the surface have been removed, vapor diffusion to the surface controls the emission rate. Therefore, Equation 1, the short-term emission rate equation, considers both the resistance of the soil to mass transfer and the resistance at the air/soil surface. The gas-phase mass transfer coefficient, k_g, is estimated using methods described in Section 2.

Loss of the waste due to first-order biodegradation is accounted for by means of an exponential term in the emission rate equations. Biodegradation and volatilization are the only mechanisms of removal considered. The biological decay time constant is calculated using Equation 15 in Table 6-8, and assumes a knowledge of the aqueous biorate for the compound of interest. Equation 15 has a factor incorporated into it to convert aqueous biorate data to land treatment values.

TABLE 6-8. IMPORTANT EQUATIONS IN THE EPA LAND TREATMENT MODEL (RTI MODEL)

1) Emission rate

a) Short-term solution ($K_{eq} D_e t/l^2 < 0.213$)

$$E = \frac{M_o}{l} \left[\frac{1}{\dfrac{\epsilon_a}{K_{eq} k_G} + \left(\dfrac{\pi t}{D_e K_{eq}} \right)^{1/2}} \right] e^{-t/t_b} \qquad (1)$$

b) Long-term solution ($K_{eq} D_e t/l^2 \geq 0.213$)

$$E = M_o \left[\frac{2K_{eq} D_e}{l^2} \right] \exp\left(- \frac{K_{eq} D_e \pi^2 t}{4l^2} - \frac{t}{t_b} \right) \qquad (2)$$

where

E = emission rate of constituent (g/cm^2-s)

M_o = initial loading of constituent on the land treatment site (g/cm^2)

l = depth to which waste is mixed in the soil (cm)

ϵ_a = volume fraction of air-filled voids in the soil (soil air-filled porosity) (dimensionless)

K_{eq} = equilibrium coefficient of constituent in the soil (dimensionless)

t = time after waste application to the land treatment site (s)

k_G = gas-phase mass transfer coefficient (cm/sec)

D_e = effective diffusion coefficient of constituent in the soil (cm^2/s)

t_b = time constant for biological decay of constituent (s^b)

2) Fraction of the compound emitted

a) Short-term solution [$t/t_b < 0.5$ and ($K_{eq} D_e t/l^2$) < 0.25]

$$F_{at} = \left(\frac{K_{eq} D_e t}{\pi l^2} \right)^{1/2} 2(1 - 1/3\, t/t_b) \qquad (3)$$

TABLE 6-8. IMPORTANT EQUATIONS IN THE EPA LAND TREATMENT MODEL (RTI MODEL) (continued)

b) Long-term solution ($K_d\ t_b \geq 0.22$)

$$F_{at} = \frac{8}{\pi^2}\left[1 + \frac{1}{K_d\ t_b}\right]^{-1}\left[1 - \exp\left(-\ K_d\ t\ -\ t/t_b\right)\right] + 0.1878 \qquad (4)$$

c) Long-term solution ($K_d\ t_b < 0.22$)

$$F_{at} = F_a\ [1 - \exp(-\ K_d\ t\ -\ t/t_b)] \qquad (5)$$

d) Very long-term solution ($t \rightarrow \infty$) ($K_d\ t_b \geq 0.62$)

$$F_a = \frac{0.811\ K_d\ t_b}{(K_d\ t_b + 1)} + 0.1878 \qquad (6)$$

e) Very long-term solution ($t \rightarrow \infty$) ($K_d\ t_b < 0.62$)

$$F_a = \left(\frac{K_{eq}\ D_e\ t_b}{l^2}\right)^{1/2} \qquad (7)$$

where

F_{at} = fraction of constituent emitted to the air at time t

K_d = modified volatilization constant (1/s)

F_a = fraction of constituent emitted to the air after a long time

3) Fraction of the compound remaining in the soil

$$F_S = (1 - F'_{at})\ e^{-t/t_b} \qquad (8)$$

where

F_S = fraction of constituent remaining in the soil

F'_{at} = fraction of material emitted to the air at time t assuming no biodegradation (F'_{at} can be estimated by setting $t/t_b = 0$ in Equations 2a through 2e whichever is appropriate).

4) Compound's equilibrium coefficient in soil

a) For oily sludges

$$K_{eq} = \frac{P^*\ MW_{oil}}{RT}\ \frac{\epsilon_a}{L} \qquad (9)$$

TABLE 6-8. IMPORTANT EQUATIONS IN THE EPA LAND TREATMENT MODEL (RTI MODEL) (continued)

b) For dilute aqueous waste

$$K_{eq} = \frac{H_C}{RT} (10^6) \frac{\epsilon_a}{\epsilon_{waste}} \qquad (10)$$

where

P^* = pure component vapor pressure of constituent (atm)

MW_{oil} = average molecular weight of the oil (g/g mol)

R = ideal gas constant, 82.1 (atm-cm^3/g mol-°K)

T = temperature of vapor in soil (°K)

L = oil or aqueous waste loading in the soil (g/cm^3)

H_c = Henry's law constant for constituent (atm-cm^3/g mol)

ϵ_{waste} = volume fraction of waste in the soil (dimensionless)

5) Initial compound loading

$$M_o = L\ 1\ C \qquad (11)$$

where

C = Concentration (weight fraction) of constituent in the oil phase or (for dilute aqueous waste) in water

6) Modified volatilization constant

$$K_d = \frac{\pi^2}{4} \frac{K_{eq}\ D_e}{1^2} \qquad (12)$$

7) Compound's effective diffusion coefficient

a) When both air and total porosity are known

$$D_e = D_a \left(\frac{\epsilon_a^{10/3}}{\epsilon_T^{2}}\right) \qquad (13)$$

b) When only air porosity is known

$$D_e = D_a\ \epsilon_a^{4/3} \qquad (14)$$

TABLE 6-8. IMPORTANT EQUATIONS IN THE EPA LAND TREATMENT MODEL (RTI MODEL) (concluded)

where

D_a = diffusion coefficient of constituent in air (cm^2/s)

ϵ_T = total porosity of the soil (equivalent to dry basis bulk density divided by soil particle density) (dimensionless)

8) Biological decay time constant

$$t_b = \frac{4.83 * 10^7}{B} \qquad (15)$$

where

B = biorate of constituent (mg VO/g-hr)

9) Waste loading in the soil

a) For oily sludges

$$L = \frac{W\, f_{oil}}{A\, l} \qquad (16)$$

b) For aqueous dilute waste

$$L = \frac{W}{A\, l} \qquad (17)$$

where

W = total waste applied to land treatment site (g)

f_{oil} = fraction by weight of applied waste that is oil (organic)

A = area of land treatment site to which waste is applied (cm^2)

The vapors diffusing through the soil are assumed to be in equilibrium at all times with the other phases. The ratio of the amount of organics in the vapor phase to the total amount of organics incorporated into the soil, Keq, is calculated using Equation 9 or 10. Because of the limited air space in the soil/waste mixture, the air porosity is considered when calculating the equilibrium coefficient, Keq. In Equations 9 and 10, partitioning of the waste is assumed to be significant between the vapor phase and only one other phase. For oily sludge, the authors explain that the fraction adsorbed to the soil is small relative to the high waste loadings expected at landfarming sites. They state further that the volatile organics in oily wastes preferentially dissolve in oil rather than water. Therefore, only the vapor and oil phases are considered and equilibrium is assumed to be controlled by Raoult's law. For dilute aqueous wastes, only the vapor and water phases are considered and Henry's law is assumed to apply.

The emission rate of a compound is affected not only by the equilibrium vapor pressure, but also by the compounds effective diffusivity. The authors present two equations for calculating the effective diffusivity, based on the compounds diffusivity in air (Equations 13 and 14 in Table 6-8). They point out that the soil air porosity varies with time. Since the variation is difficult to accurately account for in an analytical model, they suggest using average or typical soil porosity values. The diffusion coefficient is assumed to be constant with time and with change in concentration.

By integrating Equations 1 and 2 from time zero to a specific time, t, and then making some simplifying assumptions, the fraction of a compound emitted from the soil surface can be estimated. The authors present five equations (Equations 3 through 7) which apply under different specific conditions.

When a landfarming site is retilled, the emission rate increases. In order to model emissions after retilling occurs, the fraction of the compound still remaining in the soil at the time of retilling needs to be determined. Equation 8 in Table 6-8 can be used to estimate that fraction. The emission rate after retilling is calculated using Equations 1 and 2 in Table 6-8 as before. The value M_o is replaced by the value F_sM_o, however, and the time, t, is reset to zero. If waste is reapplied at the same time that the soil is retilled, then the sum of the newly-added amount and the amount remaining replaces the value M_o in the emission rate equations.

6.1.6.2 Input Requirements--

The input parameters which need to be specified are:

1) Area of site to which waste is applied (A)

2) Depth to which waste is incorporated in the soil (l)

3) Total waste applied (W)

4) Weight fraction of the compound in the oil phase for oily sludge or water phase for aqueous waste (C)

5) Fraction by weight of oil in the waste (f_{oil})

6) Average molecular weight of the oil (MW_{oil})

7) Vapor pressure of the compound (P^*)

8) Diffusion coefficient of the compound in air (D_a)

9) Henry's law constant for the compound (H_c)

10) Biorate of the compound (B)

11) Soil air-filled porosity (ϵ_a)

12) Soil total porosity (ϵ_T)

13) Volume fraction of waste in the soil (ϵ_{waste})

14) Temperature (T)

15) Gas-phase mass transfer coefficient (k_G)

The authors provide average values for a number of the input parameters. They point out that little data is available to help select the average molecular weight of the oil. According to the authors, the emission rate is not highly sensitive to this parameter, so the use of an average value is adequate. Soil air porosity and total porosity are also hard to approximate from the literature. Also, the soil air porosity changes with time, as was mentioned in Section 6.1.6.1. The authors suggest default values to use when site-specific information is not available. Biorate data for aqueous systems are provided in U.S. EPA (1987b) for a number of chemicals. These can be used to estimate the biological decay time constant when the value of t_b is not known. A default biorate is also discussed.

The authors have conducted sensitivity studies and note that results are most significantly affected by selection of individual compound properties. Operational and field parameters, particularly tilling depth, impact emissions to a lesser extent.

6.1.6.3 Output Description--

Using the equations in Table 6-8, emission rates for a compound at any specified time can be estimated. The fraction of the compound emitted and remaining up to that time can also be predicted.

6.1.6.4 Resource Requirements--

Using the average and default values discussed by the authors for input parameters, the RTI model can be applied readily for screening purposes. A site-specific application of the model would require some field and laboratory data collection.

6.1.6.5 Ease of Use--

The solution of the equations in Table 6-8 is straight forward. The help given by the authors in assigning average values to the input data makes this an easy model to use for screening purposes.

6.1.6.6 Previous Applications--

Example calculations are presented. In addition, model predictions are compared to field data from four test sites and one laboratory simulation. Estimated emissions are within an order-of-magnitude of measured data, with both overprediction and underprediction observed. Thus, the model is adequate for screening purposes. According to the authors, the RTI model and the Thibodeaux-Hwang model (1982) discussed in Section 6.1.11.1 give similar results for initial volatilization without biodegradation.

6.1.6.7 Availability/Documentation--

The RTI model is described in U.S. EPA (1987b).

6.1.7 The Environmental Protection Agency Spreadsheet CHEMDAT6

6.1.7.1 Summary--

The RTI analytical model presented in Section 6.1.6 and the oil film model presented in Section 6.1.3 have been included in a Lotus 1-2-3 spreadsheet, called CHEMDAT6 (U.S. EPA, 1987b). CHEMDAT6 is described in Section 4.4.5. Only the application of the land treatment and oil film models is addressed here.

The land treatment model in CHEMDAT6 can be used to estimate both short- and long-term emissions. Oily, dilute aqueous, and organic liquid wastes can all be considered. The effects of tilling can be accommodated by defining time periods according to the tilling schedule. For each time period, the initial concentration of the organic pollutant must be adjusted manually to reflect losses of the organic during the previous time period.

The oil film model in CHEMDAT6 can be used to estimate emissions from an oil film either on the soil surface or floating on a water surface. Only a slight difference in the input requirements distinguishes the two applications.

6.1.7.2 Input Requirements--

The land treatment model input requirements are:

1) The oil loading

2) The weight concentration of the volatile organic

3) The depth of tilling

4) The total and the air-phase porosity

5) The molecular weight of the oil

6) The time period length

7) The temperature

8) The wind speed

9) The surface area

The oil loading can either be obtained from the operator of the landfarming facility or can be calculated by hand using Equation 5 in Table 6-8.

The oil film model input includes:

1) The windspeed

2) The surface area

3) The depth of the oil layer

4) The volatile organic concentration in the oil

5) The molecular weight of the oil

6) The density of the oil

7) The temperature

8) The number of months for disposal

The last input is needed to calculate a residence time.

6.1.7.3 Output Description--

For the land treatment model, the fractions of a compound lost to the air and biodegraded are calculated both for a specified intermediate time and for the long-term. Initial short-term emission rates are also calculated. Only the fraction of a compound emitted to the air is calculated by the oil film model.

6.1.7.4 Resource Requirements--

Lotus 1-2-3 software and a personal computer are required to use CHEMDAT6.

6.1.7.5 Ease of Use--

The creators of CHEMDAT6 assume that the user has some prior experience with Lotus 1-2-3. Instructions in the user's guide are minimal and a person unfamiliar with Lotus 1-2-3 spreadsheets is likely to be confused. The new version of CHEMDAT6 is expected to improve ease-of-use. The built-in data base is a useful feature.

6.1.7.6 Previous Applications--

The RTI land treatment model in CHEMDAT6 has been compared to field and laboratory data. The results show agreement within an order-of-magnitude, which the authors of U.S. EPA (1987b) deem adequate considering the errors involved in field sampling. Agreement within an order-of-magnitude is generally considered adequate for screening purposes.

6.1.7.7 Availability/Documentation--

CHEMDAT6 is available from the EPA Office of Air Quality Planning and Standards, Research Triangle Park, N.C.

6.1.8 The Jury et al. Model

Jury et al. (1983) present a general screening model that can be used to predict volatile emissions from a dilute aqueous waste applied to the soil at a land treatment facility. The one-dimensional analytical model is described in detail in Section 7.2.1.

Cadena et al. (1989) modify the model slightly so that it can be applied to the landfarming of oily wastes. The model is adapted to oily wastes by calculating an effective Henry's law constant. Equations are proposed, based on the work of Dupont (1986), which consider the solubility of the pollutant in water and the solvent-water partition coefficient. The effective Henry's law constant, K', for single-ring aromatics is:

$$K' = 0.041S^{0.543} K_H \tag{1}$$

where

S = the compound's solubility in water (mol/L)

K_H = the dimensionless Henry's law constant

For polynuclear aromatic hydrocarbons (PAH), Cadena et al. (1989) derive the following relationship:

$$K' = K_H S^{0.617} \exp(0.00135\, t_m - 3.79) \tag{2}$$

where

t_m = melting point of the PAH (°C) or 25 °C, whichever is larger

The calculated effective Henry's law constant is used to replace the Henry's law constant in Equations 2a. and 4c. of Table 7-1. Otherwise the equations remain unchanged.

Cadena et al. compared predicted emissions from soil-incorporated oily waste with laboratory data and concluded that the modified Jury et al. model is a useful tool in estimating volatile organic emissions from landfarming operations. The many simplifying assumptions made in developing the model should be remembered, however (Section 7.2.1).

6.1.9 The Enfield et al. Model

Enfield et al. (1986) develop a screening-level model of the fate and transport of chemicals at a rapid-infiltration land treatment facility. Rapid-infiltration facilities are defined as those receiving wastewater at rates greater than 5.3 m/yr or 4 in/week. Their operation is based on periodic application of wastewater, followed by drying periods.

The Enfield et al. model sequentially solves equations for three separate compartments, which represent different stages of the rapid-infiltration land treatment process. The first compartment defines the fate of a chemical in a flooded infiltration basin. The second describes losses from volatilization and transport at the beginning of the drying cycle in a thin soil layer near the ground surface. The third compartment simulates the transport and transformation of the chemical in the soil column down to the saturated zone. The output from each compartment supplies the input for the next compartment.

The first compartment is assumed to be a completely-mixed surface impoundment. The chemical is removed from the basin via volatilization and hydrolysis. Equation 1 in Table 6-9 describes the concentration of the chemical in the basin as a function of time. The assumptions associated with the use of Equation 1 are:

1) No flow occurs in the basin.

2) Transformations are described by first-order kinetics.

3) The two-film theory of mass transfer applies.

4) No infiltration or evaporation occurs.

5) The assumed depth of the water is the actual average depth.

6) The chemical is instantly applied.

The authors solve Equation 1 for the time that the pond is in existence to determine the concentration of the chemical entering the soil. Because infiltration does in reality occur throughout the pond's existence, using this value for the time underestimates the amount of chemical entering the soil. Almost all the water will have infiltrated at a concentration higher than predicted. Perhaps a better choice would be the time when the average depth occurs.

The chemical remaining at the end of the wetting cycle is applied to the bottom of the second compartment, a thin soil layer. The soil layer acts to restrict volatilization. Quasi-steady-state diffusion in the liquid and vapor

TABLE 6-9. IMPORTANT EQUATIONS IN THE ENFIELD ET AL. MODEL

1) The concentration of the compound in the surface impoundment

$$C = C_o \exp[-(k_{t1} + k_{o1}/L)t] \tag{1}$$

where

C = concentration in the wastewater (g/g total substrate)
C_o = initial concentration in the wastewater (g/g total substrate)
k_{t1} = first-order transformation rate coefficient (1/day)
k_{o1} = overall mass transfer coefficient (m/day)
L = average depth of water in the basin (m)
t = time (day)

2) The concentration entering the third compartment

$$C_i = \frac{C\, V_d \sinh(\sqrt{\alpha}\ell)}{(1\text{-FTF})\, D^* \sqrt{\alpha} \cosh(\sqrt{\alpha}\ell) + V_d \sinh(\sqrt{\alpha}\ell)} \tag{2}$$

where

$$\alpha = k_t^*/D^* \tag{3}$$

$$k_t^* = k_{ts}k_d + (k_{t1}\theta\rho_1)/\rho_s \tag{4}$$

$$\rho_1 = V_1 \left(\frac{RCT}{R}\right) \tag{5}$$

$$D^* = D_1 + \left(\frac{k_v}{k_a}\right) \frac{D_o \eta^{10/3}}{n^2} \tag{6}$$

$$V_1 = V_d/\theta \tag{7}$$

$$R = 1 + \frac{\rho_s k_d}{\theta \rho_1} + \frac{k_v}{k_a} \tag{8}$$

and where

k_t^* = lumped first-order transformation rate (1/s)
C_i = concentration entering the third compartment (g/g total)

TABLE 6-9. IMPORTANT EQUATIONS IN THE ENFIELD ET AL. MODEL (continued)

V_d = Darcy flux of water in the third compartment (m/s)
FTF = fraction of time flooded
D^* = lumped dispersion coefficient (m^2/s)
ℓ = thickness of the second compartment (m)
k_{ts} = first-order transformation coefficient in the solid phase (1/s)
k_d = adsorption distribution coefficient (m^3/mg)
k_{tl} = first-order transformation coefficient in the liquid phase (1/s)
θ = volumetric water content
ρ_l = density of the liquid (mg/m^3)
ρ_s = density of the soil (mg/m^3)
D_l = diffusion coefficient for the liquid phase (m^2/s)
k_v = first-order liquid/vapor transfer coefficient (1/s)
k_a = first-order vapor/liquid transfer coefficient (1/s)
D_o = diffusion coefficient of the chemical in free air (m^2/s)
η = air filled porosity
n = total porosity
RCT = operational cycle of the treatment system (s)
V_l = interstitial liquid velocity (m/s)
R = lumped retardation factor

3) The concentration in the liquid phase in the third compartment at a given location and time

a) For $0 < t \leq t_o$

$$C_l(x,t) = C_{in}\,A(x,t) + C_i\,B(x,t) \tag{9}$$

b) For $t > t_o$

$$C_l(x,t) = C_{in}\,A(x,t) + C_i\,B(x,t) - C_i\,B(x,t-t_o) \tag{10}$$

TABLE 6-9. IMPORTANT EQUATIONS IN THE ENFIELD ET AL. MODEL (concluded)

where

$$A(x,t) = \exp(-\mu t/R)[\ 1 - 1/2 \ \mathrm{erfc} \left[\frac{Rx - V_1 t}{2(D^* Rt)^{1/2}}\right]$$

$$-1/2 \exp\ (V_1 x/D^*) \ \mathrm{erfc} \left[\frac{Rx + V_1 t}{2(D^* Rt)^{1/2}}\right]\ ] \qquad (11)$$

$$B(x,t) = 1/2 \exp \left[\frac{(V_1 - u)x}{2\eta^*}\right] \mathrm{erfc} \left[\frac{Rx - ut}{2(D^* Rt)^{1/2}}\right]$$

$$+ 1/2 \exp \left[\frac{(V_1 + u)x}{2D*}\right] \mathrm{erfc} \left[\frac{Rx + ut}{2(D^* Rt)^{1/2}}\right] \qquad (12)$$

$$u = V_1 \left[1 + \frac{4\mu D^*}{V_1^{\ 2}}\right]^{1/2} \qquad (13)$$

$$\mu = \rho_s k_t^* / (\theta \rho_1) \qquad (14)$$

and where

C_1 = concentration in the liquid phase (g/g)
C_{in} = initial concentration in the profile (g/g)
x = location (m)
t = time (s)
μ = transformation coefficient (1/s)
t_o = total time of application (s)

and given

$$C_1(x,0) = C_{in} \qquad (15)$$

$$C_1(0,t) = \begin{cases} C_i \text{ for } 0 < t \leq t_o \\ 0 \text{ for } t > t_o \end{cases} \qquad (16)$$

$$\partial C_1/\partial x\ (\infty,t) = 0 \qquad (17)$$

phases, first-order transformation, and overall retardation of the chemical are considered in this compartment. Water does not flow and the volumetric water content is constant. The concentration of the chemical at the land surface is assumed to be zero. Equation 2 in Table 6-9, which is based on a conservation of mass equation at the bottom of the soil layer, can be used to estimate the concentration entering the third compartment. The difference of the results from Equation 1 and Equation 2 gives an estimate of losses due to volatilization and transformation in the second compartment.

Convective-diffusive transport through the remaining soil to the water table is simulated in the third compartment. The air, water and solid phases are modeled, and local equilibrium is assumed between the liquid phases and the other two phases. All reactions between the air and solid phases are assumed to occur with the liquid phase as intermediary. Constant soil properties, flux, and water content, and first-order transformation are assumed. Transport in the vapor phase is by diffusion only and no transformations occur in the vapor phase.

The concentration of the chemical in the liquid phase can be calculated from Equation 3 in Table 6-9 for any specified time and location below the depth of the second compartment. Equation 3 is a modified version of the equation appearing in Enfield et al. (1986), which contains numerous typographical mistakes.

The authors point out that this compartmental screening model is only a rough approximation of a real system, which is a continuum. For instance, in the third compartment, the transport of the chemical to the saturated zone is affected by partitioning and vapor diffusion, yet diffusion of vapors into the soil layer above and the subsequent volatilization of the vapors are not considered. Nonetheless, the authors found favorable agreement with laboratory data for 18 compounds. Predicted volatilization values were within a factor of two of the measured data when biodegradation was included in the model.

6.1.10 Contaminated Particulate Emission Methods

6.1.10.1 The Cowherd et al. Rapid Assessment Method--

Cowherd et al. (1985) develop a methodology for predicting inhalation exposure to contaminated particulates. The procedure is designed for use in emergency response situations and thus, is expected to be accurate within an order-of-magnitude only. The emission of respirable particulates, which are defined as particles <10 μm in diameter, is considered. In addition to estimating the rate of erosion caused by wind and by traffic, the Cowherd et al. methodology also considers atmospheric dispersion of the particles and predicts human exposure. This summary will briefly discuss the estimation of erosion rates only. When these are calculated, the rate of associated contaminant emissions can be predicted.

Cowherd et al. distinguish between surfaces with unlimited erosion potential, such as bare, loose, fine soils, and surfaces with limited erosion potential. The latter type of surface can be either a crusted soil or a non-homogeneous soil containing elements that do not erode, such as rocks. The equations used to estimate particulate emissions caused by wind from these two types of surfaces are shown in Table 6-10. The solution of these equations requires the use of graphs and charts, which are provided in Cowherd et al. (1985), but which are not reproduced here. The equations are based on the assumption that emissions are continuous, steady, and uncontrolled. Therefore they are best for predicting long-term, average results.

The input required includes field observation of percent vegetative cover, the frequency of disturbance, the crusted surface characteristics, the surface aggregate size distribution, the area covered by elements that do not erode, and the roughness height of the soil. In addition, information about wind speeds and monthly precipitation and temperature are needed.

The equation presented by Cowherd et al. to estimate particulate emissions from traffic on unpaved surfaces is not shown in Table 6-10 because emissions from vehicle traffic are not expected to be significant at landfarming sites. Tilling of the soil can be a significant source of emissions, however. During tilling, the soil crust is destroyed and dust from the loosened soil enters the air. The extent of emissions depends on the soil texture, the soil moisture content and the silt content of the top 10 cm. of the soil. Cowherd et al. define silt as particles <75 μm in diameter and state that emissions increase as silt content increases. The authors present an equation to estimate dust emission resulting from tilling (Equation 3 in Table 6-10). By using different values for the particle-size multiplier, k, estimates for different particle-size ranges can be made. Note that the units of this equation differ from the units used in Equations 1 and 2.

The rate of contaminant emissions from a specific source area is estimated using Equation 4 in Table 6-10. The authors assume that the mass fraction of contaminant is known from field data collection and that the site is uniformly contaminated. In addition, the contaminant concentration associated with the respirable particles is assumed to match the bulk contaminant concentration, even though there is evidence that contaminants are primarily adsorbed by the fine size fraction of a soil (i.e., silt, clay, and humus material) (Valine, et al., 1989).

The authors present example applications of the use of their methodology. While the methods presented by Cowherd et al. estimate emissions of respirable particles only, the emission of total suspended particulates (defined by Turner et al. (1984) as particles <30 μm in diameter and by Smith et al. (1982) as particles <50 μm in diameter) can be approximated if the soil size distribution is known.

6.1.10.2 The Turner et al. Method--

Turner et al. (1984) present a method of estimating the degree of contamination (DOC) of soils from slightly-soluble hazardous waste. They combine the results with estimated particle emission rates to predict contaminant emission rates. Both a modified version of the wind erosion equation (Skidmore and Woodruff, 1968) and the Cowherd et al. (1985) method are used to estimate particulate emission rates from flat source areas.

TABLE 6-10. EQUATIONS IN THE COWHERD ET AL. METHOD RELEVANT TO THIS REPORT

1) Wind erosion of particles ≤ 10 μm in diameter from surfaces with limited erosion potential

$$E_{10} = 0.83 \frac{f\ P(u^+)\ (1-V)}{(PE/50)^2} \tag{1}$$

where

E_{10} = emission factor, i.e., annual average emission rate per unit area of contaminated surface (mg/m^2-hr)

f = frequency of disturbance per month

u^+ = observed (or probable) fastest mile of wind for the period between disturbances (m/s)

$P(u^+)$ = erosion potential, i.e., quantity of erodible particles present on the surface prior to the onset of wind erosion (g/m^2)

V = fraction of contaminated surface area covered by continuous vegetative cover (equals 0 for bare soil)

PE = Thornthwaite's Precipitation Evaporation Index used as a measure of average soil moisture content

2) Wind erosion of particles ≤ 10 μm in diameter from surfaces with unlimited erosion potential

$$E_{10} = 0.036\ (1-V) \left(\frac{[u]}{u_t}\right)^3 F(x) \tag{2}$$

where

$[u]$ = mean annual wind speed (m/s)

u_t = threshold value of wind speed at 7 m (m/s)

x = $0.886\ u_t/[u]$ = dimensionless ratio

$F(x)$ = function plotted in Cowherd et al. (1985)

3) Dust emissions from agricultural tilling

$$E = k(604)(s)^{0.6} \tag{3}$$

where

E = emission factor (kg/hectare)

TABLE 6-10. EQUATIONS IN THE COWHERD ET AL. METHOD RELEVANT TO THIS REPORT (concluded)

---

k = particle size multiplier ($k = 1.0$ when total particulates are considered. $k = 0.21$ when particles $\leq 10\ \mu m$ in diameter are considered)

s = silt content of surface soil (%)

4) Contaminant emission rate for particles $\leq 10\ \mu m$ in diameter

$$R_{10} = \alpha\ E_{10}\ A \qquad (4)$$

where

R_{10} = emission rate of contaminant (mg/hr)

α = mass fraction of contaminant emissions

A = source extent (for a specified averaging time in the case of mechanical resuspension) (m^2)

The authors provide a thorough discussion of adsorption of chemicals onto soils. Assuming that all the contaminant on the soil particles is adsorbed, they calculate the DOC as follows:

$$d = (K_{oc})(C_o)(S) \tag{3}$$

where

d = degree of contamination (mg/g soil)

K_{oc} = the adsorption coefficient (mg/g/mg/mL)

C_o = fraction of organic carbon

S = solubility of the chemical in water (mg/mL)

The compound's solubility represents an upper bound on its concentration in equilibrium with the soil and values can be found in the literature. The adsorption coefficient can be estimated using regression equations found in Lyman et al. (1982), while the soil organic carbon content should be measured. The degree of contamination can decrease over time due to biological or chemical degradation. Turner et al. present an equation which corrects the DOC for first-order decay. It assumes that the chemical's half-life is known.

$$d = d_o \exp(-0.693/t')t \tag{4}$$

where

d_o = degree of contamination at time zero (mg/g soil)

t' = half-life of the chemical (days)

t = time since application to the soil (days)

The wind erosion equation (Skidmore and Woodruff, 1968) calculates the potential annual average soil loss of all particles <840 μm in diameter, with no information regarding suspended or respirable particles. The wind erosion equation takes into account the effects of eleven variables, which are represented by five parameters as follows:

$$E = f(I', C', K', L', V) \tag{5}$$

where

E = net soil loss

I' = soil and knoll erodibility factor

C' = local wind erosion climatic factor

K' = soil ridge roughness factor

L' = field length

V = equivalent vegetative cover

The equation is a complex function of the five parameters and is solved with the use of graphs and nomograms. Turner et al. do not provide detailed information about the wind erosion equation and their example site calculations assume the reader has access to Skidmore and Woodruff's (1968) report. Given knowledge about the size distribution of the soil, the wind erosion equation can be used to calculate either the suspended or respirable particulate emission rate by multiplying the fraction of suspended or respirable particles by the net soil loss.

In addition to the wind erosion equation, Turner et al. describe the Cowherd et al. (1985) method of predicting respirable particulate emissions (see Section 6.1.10.1 of this report). Using an example site calculation, the authors found that the Cowherd et al. method predicted emissions approximately one order-of-magnitude higher than those predicted by the wind erosion equation. The authors explain that the main reason for the difference is the incorporation of a climatic factor in the wind erosion equation which is not considered in the Cowherd et al. method.

Once the particulate emission rate is calculated, it is multiplied by the DOC result to obtain an estimate of the chemical emission rate caused by particulate suspension.

6.1.11 Other Land Treatment Models

Three models which can be used to estimate air emissions from land treatment facilities are briefly summarized in this section.

6.1.11.1 The Thibodeaux-Hwang Model--

Thibodeaux and Hwang (1982) develop a simple one-dimensional steady-state model for estimating air emissions at a landfarming site after the incorporation of an oily waste into the soil. Fickian diffusion of a chemical in the gaseous phase is modeled independent of other removal processes. Thus, the model is only valid for the period after application and before biodegradation begins. An advantage of the model is that either surface application or subsurface injection can be simulated. The model assumes that no adsorption, biodegradation, or vertical movement of the oily waste occurs. The soil is assumed isothermal and transport is limited by vapor diffusion and diffusion resistance in the oil phase. The vapor concentration at the soil surface is zero. No stagnant boundary layer is modeled. The oil is assumed to be bidispersed, with part present as a film and part in clumps.

The model is based on the concept of a dried-out zone (see Figure 6.1). Initially, the entire zone of waste incorporation is wet. As the pollutant partitions into the vapor phase and diffuses upward, the soil closest to the surface becomes dry. With time the thickness of the dry zone increases and the thickness of the wet zone decreases. The dry zone is free of the compound, except for vapor diffusing from below. The time required for all

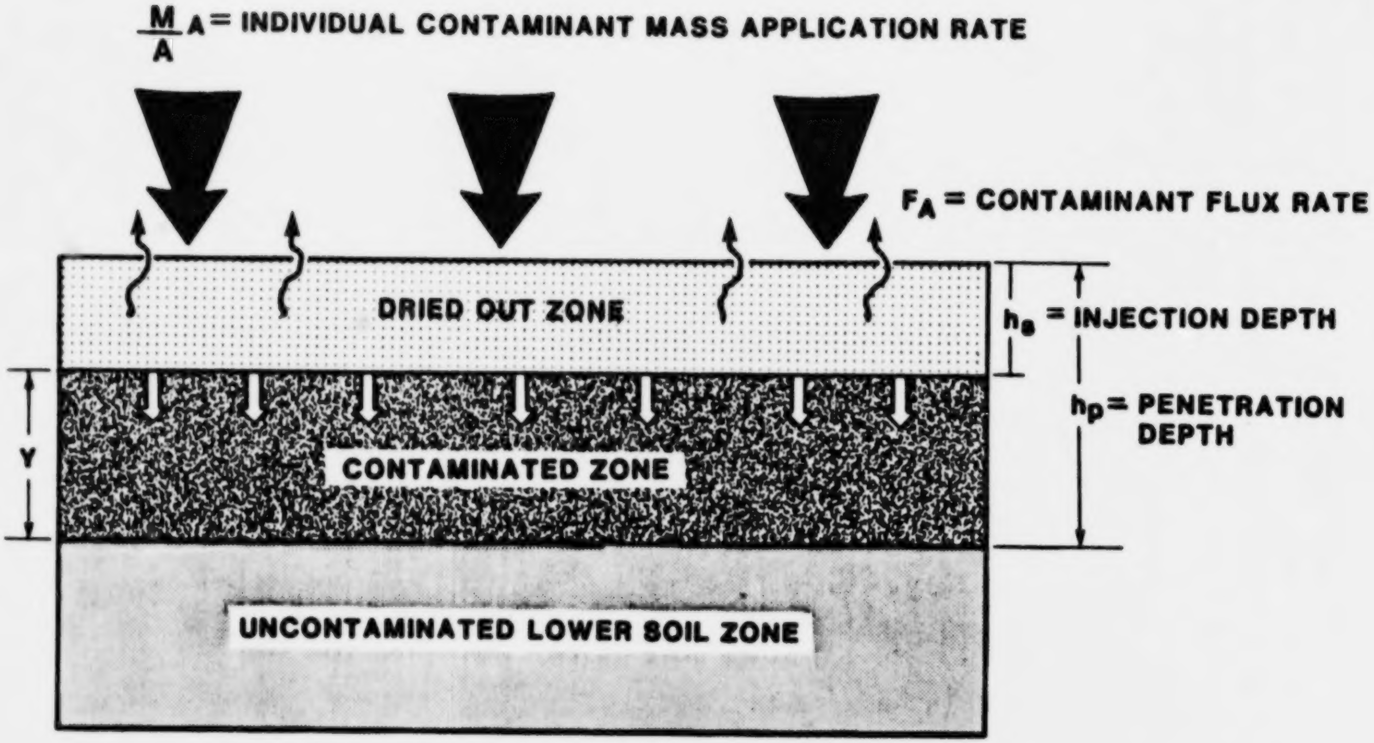
$\frac{M}{A}$A = INDIVIDUAL CONTAMINANT MASS APPLICATION RATE
F_A = CONTAMINANT FLUX RATE
DRIED OUT ZONE
h_e = INJECTION DEPTH
h_p = PENETRATION DEPTH
Y
CONTAMINATED ZONE
UNCONTAMINATED LOWER SOIL ZONE

Figure 6.1. Theoretical contaminant behavior in the Thibodeaux-Hwang model (from Dupont and Reineman, 1986).

the compound to volatilize into the soil pores is calculated using Equation 1 in Table 6-11. Mass flux is calculated with Equation 2.

The equilibrium soil vapor phase concentration (Equation 3 in Table 6-11) is related to the oil phase concentration by equating the rate of movement through each phase. The oil diffusion rate depends on the diffusion length and interfacial area (Equations 4 and 5 in Table 6-11). Cadena (1989) points out that the aûthors give no help in evaluating clump diameter and other parameters needed to solve Equation 3.

The Thibodeaux-Hwang model (1982) has been referenced and evaluated more than most models. Hwang (1982) summarizes and corrects typographical errors in the original model. Breton et al. (1984) describe the model and list the input requirements. The model is evaluated by Dupont and Reineman (1986) and Dupont (1986) using measured laboratory and field data. The predicted results correlated with the measured laboratory data by a factor of two to ten for surface application and within one to two orders-of-magnitude for subsurface injection. It was concluded that the simple diffusion model does not adequately describe subsurface application. The authors found that the model adequately predicts air emissions at field sites when detailed site-specific data are available. Cadena et al. (1989) compare the model to that of Jury et al. (1983) and conclude that the Thibodeaux-Hwang model significantly over-predicts emissions because it does not consider transport or biodegradation. Given this finding and the availability of more complete models, the Thibodeaux-Hwang model is not recommended. It is presented in this section chiefly because it is a widely-known model and because the concept of a dried-out zone has influenced other modelers.

6.1.11.2 The Seasonal Soil Compartment Model (SESOIL)--

SESOIL is a compartmental unsaturated-zone environmental-fate model (Bonazountas and Wagner, 1984b) which can be used to estimate emissions from an aqueous waste treated at a landfarming facility. For a summary of the model, refer to Section 7.2.4.

6.1.11.3 The Risk of Unsaturated/Saturated Transport and Transformation Interactions for Chemical Concentrations Model (RUSTIC)--

RUSTIC is a linked system of three submodels which simulate the fate of chemicals in the root zone, vadose zone, and saturated zone (Dean et al., 1989a; Dean et al., 1989b). The root zone submodel is capable of simulating the vapor-phase transport and volatilization of three chemicals or a parent chemical and two daughter products from an aqueous waste. RUSTIC is described in Section 7.2.5.

6.1.12 Sensitivity to Input Parameters

U.S. EPA (1987b) conducted analyses to evaluate the sensitivity of their landfarming model (RTI model in Section 6.1.6) to variations in input parameter values. The results are specific to that particular model, but are of general interest as well.

TABLE 6-11. IMPORTANT EQUATIONS IN THE THIBODEAUX - HWANG MODEL

1) Time for the initial applied mass to completely volatilize into the soil pore space

$$t_d = \frac{(h_p + h_s)}{2\ D_{ei}\ C_{ig}} \left[\frac{m_{io}}{A}\right] \tag{1}$$

where

t_d = dry-out time (s)

h_p = depth of soil contamination below the surface (cm)

h_s = depth of subsurface injection (cm)

m_{io} = initial amount of component i applied (g)

D_{ei} = effective diffusivity of component i in the air-filled soil pores (cm^2/s)

C_{ig} = equilibrium gas-phase concentration of component i at the oil-gas interface in the soil pores (g/cm^3)

A = surface area (cm^2)

2) Mass flux of each component at a specified time

$$q_i = \frac{D_{ei}\ C_{ig}}{\left[{h_s}^2 + \dfrac{2\ D_{ei}\ t\ A(h_p - h_s)\ C_{ig}}{m_{io}}\right]^{\frac{1}{2}}} \tag{2}$$

where

q_i = rate of emission of component i (g/cm^2-s)

t = time (s)

3) Equilibrium soil vapor phase concentration of component i

$$C_{ig} = \left[\frac{H_c}{1 + H_c \dfrac{6D_{ei}\ Z_o}{D_{wi}a_s({h_p}^2 + h_p\ h_s - 2{h_s}^2)}}\right] C_{iwo} \tag{3}$$

TABLE 6-11. IMPORTANT EQUATIONS IN THE THIBODEAUX - HWANG MODEL (concluded)

where

H_c = modified Henry's law constant (cm^3 oil/cm^3 air)
Z_o = oil-layer diffusion length (cm)
D_{wi} = effective diffusivity of component i in the waste (cm^2/s)
a_s = interfacial area per unit volume of soil (cm^2/cm^3)
C_{iwo} = initial concentration of component i in the oily waste (g/cm^3)

4) For film-form oil

$$a_s = 6/d_p \tag{4}$$

$$Z_o = \frac{d_p \bar{\rho}_p w_f}{6\bar{\rho}_w} \tag{5}$$

where

d_p = soil clump diameter (cm)
$\bar{\rho}_p$ = soil clump density (2.65 g/cm^3)
w_f = fraction of oil in film-form on the soil
$\bar{\rho}_w$ = waste-oil density (g/cm^3)

5) For lump-form oil

$$a_s = 2.7/d_p \tag{6}$$

$$Z_o = d_p/2 \tag{7}$$

6) Mass fraction of oil in film form

$$w_f = \frac{0.5\ M_T}{h_p \bar{\rho}_B A} \tag{8}$$

where

M_T = total amount of applied waste (g)
$\bar{\rho}_B$ = bulk soil density (g/cm^3)

The studies indicate that the properties of the modeled waste constituents, such as the vapor pressure, diffusivity, and biodegradation half-life, have the most significant impact on results. Volatile organics are chiefly emitted to the air, unless the biodegradation rate is increased or the diffusivity is decreased. The depth to which the waste is tilled affects volatilization. The average molecular weight of the oil also affects air emissions. As the average molecular weight increases, the fraction of the constituent volatilized increases. Finally, increasing waste loading also increases air emissions.

Cadena et al. (1989), using the modified version of the Jury et al. (1983) model described in Section 6.1.8, found that adsorption does not affect the emission of volatile organics from oily waste. On the other hand, he showed that the transport of soluble pollutants has a very important effect. Evaporation aids the process of diffusion and volatilization, whereas infiltration hinders volatilization.

Hwang (1982) states that the following parameters have an important effect on air emissions: soil type, humidity, waste loading, temperature, wind, and application model. He further states that barometric pumping and thermal diffusion affect the emission rate, but their importance relative to diffusive transport is not clearly known.

6.2 COMPOSTING MODELS

The composting process was introduced in Section 3.4.2. As was mentioned in that section, the use of composting techniques to treat toxic wastes is a new technology, which is still being researched. An adequate data base describing the complex reactions involved is still lacking. In preparing this report, no mathematical model of the fate of hazardous compounds during the composting process was identified in the literature. Conversations with experts on composting confirmed that mathematical models are not available.

Hogan et al. (1989) constructed a laboratory physical model of field-scale composting piles. They point out that the factors of overriding concern in determining system behavior are the generation and transfer of heat. These factors affect gaseous diffusion, oxygen availability, and moisture content. According to the authors, the only practical way of controlling the composting process is to remove heat by means of ventilation.

These facts point to the need to use closed vessel systems when treating volatile and semi-volatile organic compounds. Increases in temperature affect Henry's law constant and will increase emissions of semi-volatiles (i.e., chemicals for which gas-phase mass transfer resistance is significant in calculating the overall mass transfer coefficient). Both the stripping and leaching of toxic compounds can be controlled in closed-vessel systems and the gases produced can be further treated. Until data are available on the magnitude of emissions from open-pile systems, the use of closed systems is recommended.

6.3 SOIL FILTER BED (BIOFILTER) MODELS

6.3.1 Introduction

Although soil filter beds are a proven technology in the control of odors and have been used successfully to remove toxic vapors from gas streams (see Section 3.4.3), the literature on this process is sparse. Telephone contact with people researching biofilters in the United States indicates that experiments with physical models are currently being conducted in order to define the operational characteristics of the system.

The Europeans have more experience with soil filter beds. The only mathematical model of a biofilter identified for this report was developed by researchers in the Netherlands (Ottengraf and van der Oever, 1983). The model was developed for use in conjunction with laboratory research and can not be easily applied for regulatory screening purposes. Nonetheless, it provides useful insight into the biokinetics of soil filter beds.

Clearly, there is a need for further research before the magnitude of hazardous emissions from biofilters can be estimated easily from mathematical models. At this time, field monitoring and, if necessary, further treatment of the gases emitted from existing individual biofilters is necessary.

6.3.2 The Ottengraf-van den Oever Model

6.3.2.1 Summary--

Ottengraf and van den Oever (1983) describe a mathematical model which can be used to predict the capacity of a soil filter bed to eliminate specific compounds. The biodegradation by microorganisms in biolayers coating the particles in a support medium is the only elimination process considered. The authors make the following assumptions in developing their model:

1) Gas-phase resistance at the gas/biolayer interface is negligible. Therefore the concentration of the compound in the biolayer at the interface is in equilibrium with the bulk gas-phase concentration.

2) The biolayer thickness is small relative to the diameter of the support-medium particles.

3) In the biolayer, nutrient transport is controlled by diffusion, which is described by an effective diffusion coefficient.

4) Utilization of the compound in the biolayer is described by zero-order kinetics. Experiments conducted by the authors confirm this assumption.

5) Gas flow is described as plug flow.

6) The concentration of the compound in the inflowing gas is constant.

7) The gas enters the soil filter bed at a height equal to zero and exits at a height equal to the thickness of the support-medium layer.

8) Humidity is held constant at a value between 50 to 70 percent.

All of these assumptions are reasonable for a typical soil filter bed.

The authors distinguish between two different operational conditions. In the first situation, the diffusion of nutrients through the biolayer does not limit biological activity. The entire thickness of the biolayer is active and elimination of a compound is controlled only by the biological reaction rate. This situation, described by the solid line in Figure 6.2, is defined as reaction limited. In Figure 6.2, C_g is the concentration in the gas phase, C is the concentration in the liquid phase, and M is the equilibrium distribution coefficient.

The second case, indicated by the dashed line in Figure 6.2, is possible at low gas-phase concentration levels. Because the diffusion rate is small relative to the biological reaction rate, the substrate does not penetrate the full thickness of the biolayer. The part of the biolayer closest to the support medium is inactive and the condition is described as diffusion limited.

For each situation, the authors solve a gas-phase mass balance on the substrate. The results are shown in Equations 1 and 5 of Table 6-12. These equations can be used to estimate the concentration of a compound in the gas exiting a soil filter bed. Equation 1 predicts a linear relationship between concentration and height in the soil filter bed. The relationship predicted by Equation 5 is non-linear. The fraction of the compound removed by the biolayer can be estimated from Equation 2. Equation 3 represents the critical value that determines when diffusion-limited conditions begin to influence results. Equation 4 calculates the thickness of the substrate penetration layer when diffusion is limiting.

6.3.2.2 Input Requirements--

The input parameters needed for the reaction limited case are:

1) The inflowing gas-phase concentration (C_{go})

2) The biolayer surface area per volume (A_s)

3) The surficial gas velocity (Ug)

4) The zero-order reaction rate constant (k)

5) The height of the soil filter bed (H)

6) The total biolayer thickness (δ)

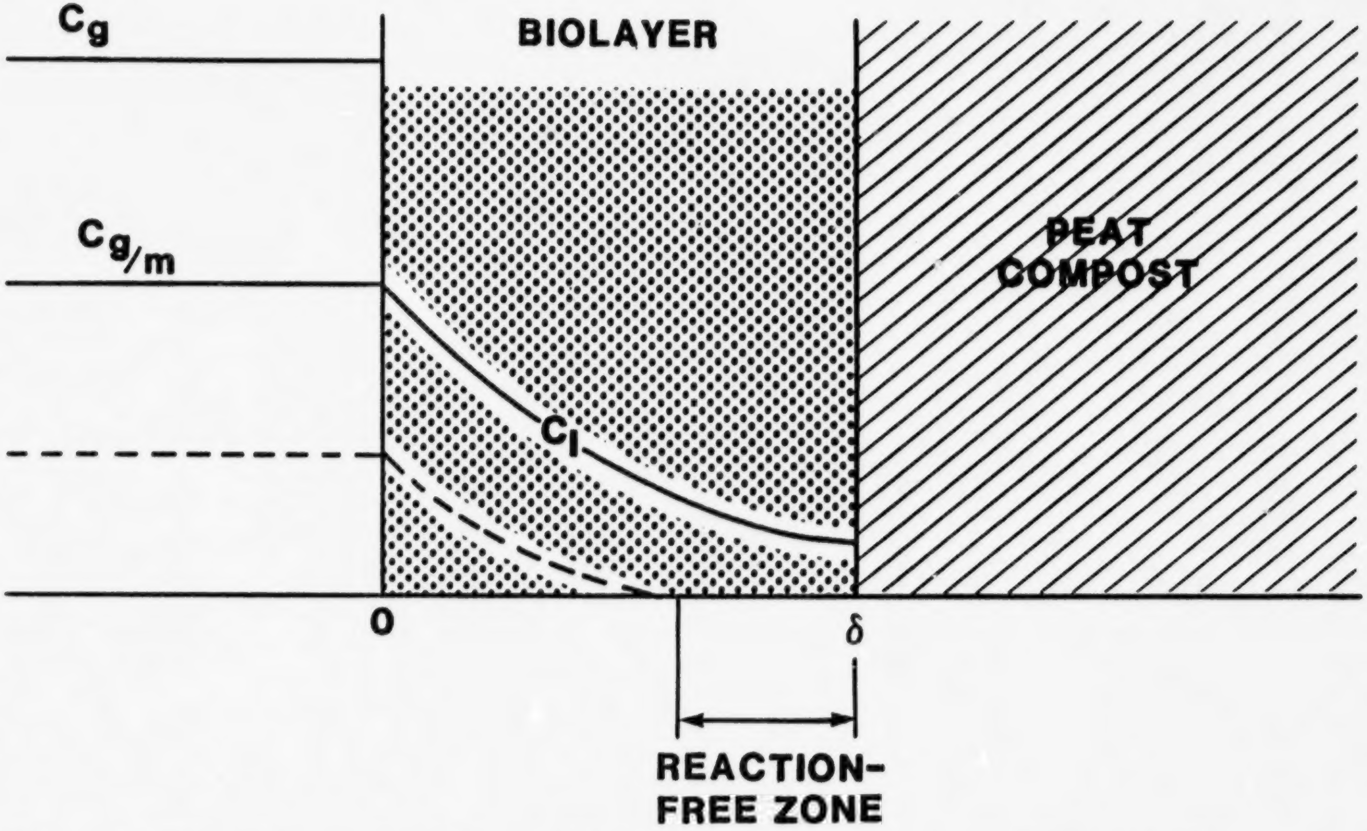
C_g
BIOLAYER
$C_{g/m}$
PEAT COMPOST
C_l
0
δ
REACTION-
FREE ZONE

Figure 6.2. Possible concentration profiles in the biolayer of a soil-filter bed (from Ottengraf and van den Oever, 1983).

TABLE 6-12. IMPORTANT EQUATIONS IN THE OTTENGRAF AND VAN DEN OEVER MODEL

For reaction limited cases

1) Solution to a gas-phase mass balance on the substrate

$$\frac{C_{ge}}{C_{go}} = 1 - \frac{A_s \, k \, \delta \, H}{C_{go} \, U_g} \tag{1}$$

where

C_{ge} = exit gas-phase concentration (g/m^3)
C_{go} = inlet gas-phase concentration (g/m^3)
A_s = biolayer surface area per volume (m^2/m^3)
k = zero-order reaction rate constant per unit volume of biolayer (g/m^3-s)
δ = total biolayer thickness (m)
H = height of the biofilter (m)
U_g = surficial gas velocity (m/s)

2) Degree of conversion

$$f = 1 - \frac{C_{ge}}{C_{go}} = \frac{A_s \, k \, \delta \, H}{C_{go} \, U_g} \tag{2}$$

For diffusion limited cases

3) Critical value of Thiele number

$$\phi_{cr} = \delta \left(\frac{k \, m}{D' C_g}\right)^{\frac{1}{2}} = \sqrt{2} \tag{3}$$

where

ϕ_{cr} = Thiele number (critical value which determines if a reaction-free zone exists)
m = distribution coefficient = $(C_g/C_l)_{equilibrium}$
C_g = gas-phase concentration (g/m^3)
C_l = liquid-phase concentration (g/m^3)
D' = effective diffusion coefficient in the biolayer (m^2/s)

TABLE 6-12. IMPORTANT EQUATIONS IN THE OTTENGRAF AND VAN DEN OEVER MODEL (concluded)

4) Penetration thickness in the biolayer

$$\lambda = \left(2\frac{D' \ C_g}{k \ m}\right)^{1/2} \qquad (4)$$

where

λ = penetration or effective biolayer thickness (m)

5) Solution to the gas-phase mass balance on the substrate

$$\frac{C_{ge}}{C_{go}} = \left[1 - \frac{A_s \ H}{U_g} \left(\frac{k \ D'}{2C_{go} \ m}\right)^{1/2}\right] \qquad (5)$$

For the diffusion limited case, the parameters in 1 through 5 are needed, as well as two additional parameters. They are:

7) The equilibrium distribution coefficient (m)

8) The effective diffusion coefficient in the biolayer (D')

The parameters related to the biological elimination process need to be determined experimentally. Table 6-13 shows some parameter values presented by the authors from their specific experimental results. The total biolayer thickness values in Table 6-13 were calculated using Equation 3 in Table 6-12.

TABLE 6-13. PARAMETER VALUES AT A CONSTANT LOADING OF 90 g/m^3-hr

Component	m	k (g/m^3 hr)	D' (M^2/s)	C_g (g/m^3)	δ (mm)
Toluene	0.2700	50	0.85×10^{-9}	3.0	1.2
Butylacetate	0.0085	55	0.80×10^{-9}	0.2	1.5
Ethylacetate	0.0051	45	1.0×10^{-9}	0.2	.5

6.3.2.3 Output Description--

With the correct input data, the equations in Table 6-12, can be used to predict the concentration of a compound remaining in gas which has passed through a biofilter. When that value is known, the fraction of the compound removed by biodegradation can be easily determined.

6.3.2.4 Resource Requirements--

In order to predict the elimination capacity of a biofilter, experimental studies of the biokinetics of the system need to be conducted. Because interest in using soil filter beds to treat hazardous organics is new, there is little relevant literature and published data are sparse. Kampbell et al. (1987) present biodegradation rates for soil filter beds. If data are available, the equations in the Ottengraf and van den Oever model can be readily solved by hand.

6.3.2.5 Ease of Use--

The model provides insight into the biokinetics of soil filter beds and is useful for researchers. It can not be easily used by regulators.

6.3.2.6 Previous Applications--

The authors use this model in the context of their laboratory studies. No field application has been made.

6.3.2.7 Availability/Documentation--

The model and associated experimental studies are described in Ottengraf and van den Oever (1983).

SECTION 7

MODELS OF THE IN-SITU SUBSURFACE

7.1 INTRODUCTION

The realization in recent years that active microbial populations function far below the land surface has sparked interest in understanding the conditions under which these microorganisms biodegrade the toxic organic compounds which pollute many subsurface environments. In order to predict the fate of organic pollutants, models which accurately incorporate not only their transport and abiotic attenuation, but also their biotransformation, are needed.

Complex interactions between physical, chemical and biological processes exist in subsurface environments. For example, biodegradation can alter pH, which in turn can trigger chemical reactions such as hydrolysis or redox reactions. Biological growth can reduce permeability, which affects transport processes. The models developed thus far have, out of necessity, made many simplifying assumptions about the processes affecting the fate of pollutants in the subsurface. As a result, the models are best used for screening-level purposes Models of the subsurface normally consider either the unsaturated or the saturated zone, and that classification is used in this report.

The models described in this section were developed to estimate the fate of pollutants under natural conditions and do not specifically simulate in-situ bioremedial activity, such as efforts to increase the supply of nutrients and oxygen, or to alter the temperature or pH (see Section 3.5).

For the unsaturated zone models, only very limited bioremedial measures can be simulated. The application of dissolved nutrients at the surface could perhaps be simulated as a constant recharge and an increased biodegradation rate. All of the models, however, assume that vapor transport is limited to one-dimensional, vertical diffusion. The use of an aeration system would result in advective gaseous transport and would invalidate these models. The fate of a pollutant during in-situ landfarming can, of course, be simulated using methods described in Section 6.1. Analytical methods developed by Jury et al. (1983) and by Bomberger et al. (1983) and the computer models, SESOIL (Bonazountas and Wagner, 1984a) and RUSTIC (Dean et al., 1989a), can all be used to predict the fate of an aqueous waste. The Baehr-Corapcioglu (1987) model considers the fate of constituents of an oil phase, which is immobilized below the soil surface.

All the unsaturated zone models, except for RUSTIC, assume the soil is homogeneous. In reality, all soils are inhomogeneous, and diffusion of vapors through the soil is controlled by the most retarding layer (Swallow and

Geschwend, 1983). RUSTIC allows the modeling of vertical inhomogeneity. Other factors which may affect the rate of volatile emissions, are variations in temperature and in barometric pressure. Of the models reviewed in this section, only RUSTIC simulates the effect of soil temperature variations on volatilization.

All the models assume that vapor diffusion is described by Fick's law. Thorstenson and Pollock (1989) present research indicating that for multi-component gas transport in the unsaturated zone, Fick's law may not apply when non-atmospheric gases are a significant fraction of the total gas phase. They point out that very small pressure gradients in natural systems can produce viscous fluxes greater than diffusive fluxes. For present-day screening-level modeling efforts, Fick's law provides an adequate description of diffusion, but these facts should be remembered when developing more sophisticated models in the future.

A number of models which simulate the transport and biodegradation of contaminants in the saturated zone were identified for this report. These models can be used to model in-situ bioremediation of the saturated zone. However, the models provide no direct help in estimating the likelihood or magnitude of volatile emissions from the saturated zone. Only one paper (Swallow and Geschwend, 1983) discusses air emissions from a contaminated aquifer. However, the equations in that paper do not consider biodegradation, adsorption, or the aqueous flux in the unsaturated zone, and thus, do not adequately predict emissions.

7.2 UNSATURATED ZONE MODELS

7.2.1 The Jury et al. Model

7.2.1.1 Summary--

Jury et al. (1983) present a general one-dimensional analytical model for screening the fate of a trace organic chemical applied to the soil. The effects of volatilization, transport through leaching and evaporation, degradation and adsorption are considered. The authors have made a number of simplifying assumptions in developing their screening model. Applying these assumptions, which are discussed below, to the mass balance shown in Equation 1 of Table 7-1, the authors obtain analytical solutions which predict the chemical concentration at any given depth and time and the volatilization flux as a function of time (Equations 7 and 8 in Table 7-1).

The assumptions are:

1) The contaminant is assumed to exist in three-phases--a vapor, a liquid, and an adsorbed solid. Liquid/vapor and liquid/solid partitioning is described by linear equilibrium isotherms. The use of a linear adsorption isotherm is generally considered valid at low chemical concentrations. The authors suggest that the adsorption coefficient, K_D in Equations 2a. and 2b. of Table 7-1, be approximated as the product of the soil organic carbon content and the organic carbon partition coefficient. They state that this

TABLE 7-1. IMPORTANT EQUATIONS IN THE JURY ET AL. MODEL

1) Mass balance

$$\frac{\partial C_T}{\partial t} + \frac{\partial J_s}{\partial Z} + \mu C_T = 0 \qquad (1)$$

where

C_T = total concentration (g/m^3soil)
J_s = solute mass flux (g/m^2-day)
μ = first-order degradation rate constant (1/day)
Z = depth (m)
t = time (day)

2a) Liquid-phase partition coefficient

$$R_L = \rho_b K_D + \theta + a K_H \qquad (2)$$

2b) Gas-phase partition coefficient

$$R_G = \rho_b K_D/K_H + \theta/K_H + a \qquad (3)$$

where

R_L = liquid-phase partition coefficient
R_G = gas-phase partition coefficient
ρ_b = soil bulk density (kg/m^3)
θ = volumetric liquid content
a = volumetric air content
K_H = dimensionless Henry's law constant
K_D = linear adsorption coefficient (m^3/kg)

3) Effective solute convective velocity

$$V_E = I - E/R_L \qquad (4)$$

where

V_E = effective solute convective velocity (m/day)
I = infiltration rate (m/day)
E = evaporation rate (m/day)

TABLE 7-1. IMPORTANT EQUATIONS IN THE JURY ET AL. MODEL (continued)

4a) Soil-gas diffusion coefficient

$$D_G = \frac{a^{10/3}}{\phi^2} D_G^{air} \tag{5}$$

4b) Soil-water diffusion coefficient

$$D_L = \frac{\theta^{10/3}}{\phi^2} D_L^{water} \tag{6}$$

4c) Effective diffusion coefficient

$$D_E = (K_H \; D_G + D_L)/R_L \tag{7}$$

where

D_G = soil-gas diffusion coefficient (m^2/day)

ϕ = $(a + \theta)$ = soil porosity

D_G^{air} = air-gas diffusion coefficient (m^2/day)

D_L = soil-water diffusion coefficient (m^2/day)

D_L^{water} = water-liquid diffusion coefficient (m^2/day)

D_E = effective diffusion coefficient (m^2/day)

5) Stagnant air boundary layer thickness (Cadena, 1989)

$$d = 2.38 * 10^{-7} \; (100 - H_r)/E \tag{8}$$

where

d = stagnant air boundary layer thickness at 25°C (m)

H_r = relative humidity (%)

6) Transport velocity across the boundary layer

$$H_E = \frac{D_G^{air}}{d \; R_G} \tag{9}$$

where

H_E = boundary layer transport velocity (m/day)

TABLE 7-1. IMPORTANT EQUATIONS IN THE JURY ET AL. MODEL (concluded)

7) Total chemical concentration for a given depth, Z, and time, t

$$C_T(Z,t) = \frac{1}{2} C_o \exp(-\mu t) \left[\left\{ \mathrm{erfc}\left[\frac{Z - L - V_E\, t}{(4D_E\, t)^{1/2}}\right] - \mathrm{erfc}\left[\frac{Z - V_E\, t}{(4D_E\, t)^{1/2}}\right] \right\} \right.$$

$$+ (1 + V_E\, H_E) \exp(V_E\, Z/D_E) \left\{ \mathrm{erfc}\left[\frac{Z+L+V_E\, t}{(4D_E\, t)^{1/2}}\right] - \mathrm{erfc}\left[\frac{Z + V_E\, t}{(4D_E\, t)^{1/2}}\right] \right\}$$

$$+ (2 + V_E/H_E) \exp\{[H_E(H_E + V_E)t + (H_E + V_E)Z]/D_E\}$$

$$\left\{ \mathrm{erfc}\left[\frac{Z + (2H_E + V_E)t}{(4D_E\, t)^{1/2}}\right] - \exp(H_E\, L/D_E) \right.$$

$$\left. \left. \mathrm{erfc}\left[\frac{Z + L + (2H_E + V_E)t}{(4D_E\, t)^{1/2}}\right] \right\} \right] \qquad (10)$$

where

C_o = the initial concentration in the soil (g/m^3soil)

L = depth of incorporation below the surface (m)

8) Volatilization flux at the surface for a given time, t

$$J_s(0,t) = \frac{1}{2} C_o \exp(-\mu t) \left[V_E \left\{ \mathrm{erfc}\left[\frac{V_E\, t}{(4D_E\, t)^{1/2}}\right] - \mathrm{erfc}\left[\frac{L + V_E\, t}{(4D_E\, t)^{1/2}}\right] \right\} \right.$$

$$+ (2H_E + V_E) \exp[H_E(H_E + V_E)t/D_E] \left\{ \exp(H_E\, L/D_E) \right.$$

$$\left. \left. \mathrm{erfc}\left[\frac{L + (2H_E + V_E)t}{(4D_E\, t)^{1/2}}\right] - \mathrm{erfc}\left[\frac{(2H_E + V_E)t}{(4D_E\, t)^{1/2}}\right] \right\} \right] \qquad (11)$$

method reduces variability between soils for a given chemical because chemicals generally adsorb only to the soil organics. Linear liquid/vapor partitioning is described by Henry's law, which is known for many chemicals .

2) The net degradation of the contaminant from all decay processes in all the phases is considered to be a first-order process. In the soil, biological activity is normally the chief decay mechanism. Degradation, which is represented by the exponential terms in Equations 7 and 8 of Table 7-1, is difficult to accurately model. As have been discussed in Section 2, reported values for the degradation rate constant, μ, vary greatly and should be used with caution.

3) A homogeneous soil column of infinite depth is modeled. As a result, soil properties, such as bulk density, porosity and organic carbon content are constant.

4) The convective flow of water, either upward or downward in the soil column, is assumed to be steady, resulting in constant values for the volumetric liquid and air content. Also, dispersion is ignored.

5) The modeled contaminant is assumed to be instantaneously and uniformly incorporated in the soil to a user-specified depth, L. The incorporated contaminant does not affect the soil characteristics. It is assumed the chemical does not precipitate.

6) The flux of both water vapor and contaminant vapor from the soil surface to the atmosphere is assumed to be controlled by diffusion through a stagnant air boundary layer at the surface. The thickness of the stagnant air layer is a function of the relative humidity and the evaporation rate.

In developing an equation to calculate the stagnant air boundary layer thickness, four additional assumptions were made. These are:

1) The water vapor density at the soil surface is saturated.

2) The concentration of the chemical in the air above the stagnant layer is zero.

3) The steady-state evaporation rate is half the typical evaporation rate, because evaporation at night is negligible.

4) The stagnant layer has a minimum thickness of 0.00475 meters.

7.2.1.2 Input Requirements--

The needed input parameters are:

1) The volumetric air content of the soil pores (a)

2) The volumetric water content of the soil pores (θ)

3) The soil bulk density (ρ_b)

4) The organic carbon content of the soil (f_{oc})

5) The evaporation rate (E)

6) The infiltration rate (I)

7) The depth of incorporation (L)

8) The initial concentration in the soil (C_o)

9) Henry's law constant for the contaminant (K_H)

10) The organic carbon partition coefficient for the contaminant (K_{oc})

11) The contaminant's air-gas diffusion coefficient (D_G^{air})

12) The contaminant's water-liquid diffusion coefficient (D_L^{water})

13) The first-order degradation rate constant (μ)

14) The relative humidity (H_r)

If the Jury et al. model is used for the purposes it was intended (i.e. as a screening tool to classify chemicals according to their expected fate), representative values for all the input parameters can be obtained from the literature. The authors point out that few data exist for the diffusivities. These values vary little for pesticides. For pesticides or chemicals of similar molecular weight, the authors suggest a value of 0.43 m^2/day for D_G^{air} and a value of 4.3×10^{-5} m^2/day for D_L^{water}. As has been discussed previously, published values for the degradation rate constant should be used with care and some skepticism. If a site-specific application is desired by the user the basic soil properties and degradation rate constant need to be experimentally determined.

7.2.1.3 Output Description--

After the input parameters are used to solve Equations 2 through 6 in Table 7-1, Equation 7 can be solved for the total concentration at a user-specified time and depth. Equation 8 yields the volatilization flux of the solute at a specified time.

7.2.1.4 Resource Requirements--

The solution of this analytical model is possible using a calculator and tabled values for the complementary error function (erfc). The equations can also be solved more conveniently on personal computers (PC). Cadena et al. (1989) point out that overflow errors can occur from calculating the equations on a PC because mixed exponential and erfc terms are being evaluated.

7.2.1.5 Ease of Use--

The Jury et al. model can be readily applied to evaluate the behavior of one chemical relative to another in a standardized and simplified environmental scenario.

7.2.1.6 Previous Applications--

Jury et al. (1983) illustrate the use of the model for screening purposes with output for two pesticides, lindane and 2,4-D. The two pesticides, which have very different Henry's law (K_H) and organic carbon (K_{oc}) coefficients, are predicted to have different fates when applied to the soil.

Cadena et al. (1989) have compared a slightly modified version of the Jury et al. model to the Thibodeaux-Hwang model (described in Section 6.1.11.1). The laboratory data of Dupont (1986) for land application of oily wastes were used to evaluate the models. Cadena et al. concluded that the modified Jury et al. model provided a more accurate representation of the results than the Thibodeaux-Hwang model. Model predictions were similar when biodegradation, evaporation, and leaching were ignored. For a description of the modification made by Cadena et al., see Section 6.1.8.

7.2.1.7 Availability/Documentation--

The model is developed in Jury et al. (1983). It is described and discussed in Cadena et al. (1989).

7.2.2 The Bomberger et al. Screening Method

7.2.2.1 Summary--

Bomberger et al. (1983) present a simple screening method to determine the one or two dominant mechanisms affecting the fate of a chemical in shallow soils. The method, which can be performed quickly and inexpensively, relies on equations which roughly quantify the extent of volatilization and leaching at the soil/air interface, and on published data for the chemical and biological transformation rates. The authors suggest that this method is best used for preliminary risk assessment or for selecting which among the more complete models is appropriate for a specific study.

The chemical is assumed to exist in three phases--air, water, and solid. No immiscible liquid phase is considered. Equilibrium conditions are assumed to exist. Partitioning between the water and air phases is described using Henry's law constant and partitioning between the solid and water phases is described using the product of the soil organic carbon adsorption partition coefficient with the fraction of organic carbon in the soil (see Equation 1 in Table 7-2). The use of these equilibrium partition coefficients implies that the chemical is present at low concentrations in the soil. The assumption of equilibrium may not be valid, in which case this methodology will tend to overpredict air emissions.

TABLE 7-2. IMPORTANT EQUATIONS IN THE BOMBERGER ET AL. SCREENING METHOD

1) Total amount of material in the soil

$$\text{Total} = V\,C_A\,(\theta_A + \frac{\theta_w}{H} + \frac{\rho\,K_{oc}\,f_{oc}}{H}) = V\,C_A\,\alpha \qquad (1)$$

where

$$\alpha = \theta_A + \frac{\theta_w}{H} + \frac{\rho\,K_{oc}\,f_{oc}}{H}$$

and where

V = soil volume (cm^3)
θ_A = volume fraction of air in the soil
θ_w = volume fraction of water in the soil
ρ = soil bulk density (g/cm^3)
H = dimensionless Henry's law constant
C_A = gas phase concentration (g/cm^3)
K_{oc} = partition coefficient for soil organic carbon (cm^3/g)
f_{oc} = organic fraction of the soil

2) Change in concentration caused by diffusion in the air phase

$$\frac{\partial C_A}{\partial t} = \frac{D^A\,T_A}{\alpha}\,\frac{\partial^2 C_A}{\partial z^2} \qquad (2)$$

where

D^A = diffusion coefficient in free air (cm^2/s)
T_A = correction for the porosity of the soil
z = direction normal to the soil surface (cm)
t = time (s)

3) Correction for porosity

$$T_A = \frac{\theta_A^{10/3}}{(\theta_A + \theta_w)^2} \qquad (3)$$

TABLE 7-2. IMPORTANT EQUATIONS IN THE BOMBERGER ET AL. SCREENING METHOD (concluded)

4) Half-life for diffusion

$$t_{1/2} = \frac{L^2}{4.16 \left(\frac{D^A T_A}{\alpha}\right)} \tag{4}$$

where

$t_{1/2}$ = time when half of the chemical remains in the soil (s)

L = depth from the surface to which the chemical is initially found (cm)

5) Depth to which the maximum concentration of chemical penetrates in the soil

$$D_c = \frac{D_w}{\rho \; K_{oc} \; f_{oc}} \tag{5}$$

where

D_c = depth of the maximum chemical concentration (cm)

D_w = depth of water applied to the soil surface (cm)

The authors assume that for volatile compounds, emissions to the air are controlled by diffusion through the soil pores in the air phase (Equation 2 in Table 7-2). The factor α in Equation 2 corrects for the fact that the chemical is partitioned between three phases. The authors discuss several assumptions made in developing Equation 2. In addition to the assumption of equilibrium, it is assumed:

1) The diffusion coefficient and the porosity correction in Equation 3 are constant.

2) No transport by water movement occurs. This assumption is valid only for volatile chemicals at shallow depths, for which the expected half-life is on the order of hours to days.

3) Diffusion occurs only in the air phase.

4) Adsorption is reversible. This assumption may be incorrect in the field. If adsorption is actually irreversible, this assumption will tend to overpredict air emissions.

5) The soil does not dry out. Research indicates that the soil organic carbon partition coefficient, K_{oc}, increases in value when soils become dry. Because the value of K_{oc} affects the rate of diffusion (see Equation 2), this assumption will overpredict air emissions if soils dry out in the field.

A solution to a non-steady-state diffusion model (Farmer and Letey, 1974) is used to determine an expression for the half-life of diffusion. (Equation 4 in Table 7-2). The non-steady-state model is based on the assumptions that the chemical is uniformly mixed into the soil from the surface to a depth, L, that the concentration at the surface is zero, and that diffusion occurs both upward and downward in the soil column.

Diffusion of non-volatile chemicals in the water phase is expected to be slow and water movement due to evaporation or infiltration is expected to be the principal transport mechanism. The authors use a simple analytical equation to express mass transport. The equation considers only advection and the effect of adsorption on the rate of movement; diffusion and dispersion are ignored. In addition, it is assumed that 1) no chemical is in the soil initially, and 2) the chemical is applied to the surface and is transported into the soil by water applied at the surface. The solution to the equation is not presented. Rather, the major features of the solution are discussed. The two important conclusions are 1) that the equilibrium adsorption coefficient, $K_{oc}f_{oc}$, influences the depth of maximum concentration, but not the value of that concentration, and 2) that the adsorbed chemical moves downward, with the depth of maximum adsorbed concentration occurring at about the same depth as that of the maximum dissolved concentration. The authors use these conclusions to develop an equation to estimate the depth to which the maximum concentration of dissolved chemical penetrates (Equation 5 in Table 7-2). The equation assumes that all the chemical at the surface has dissolved.

The Bomberger et al. screening method consists of comparing the results of Equations 4 and 5 with published transformation data for oxidation, hydrolysis, photolysis, and biodegradation, in order to determine the relative importance of each mechanism.

7.2.2.2 Input Requirements--

To solve Equations 4 and 5 in Table 7-2, the following parameters are needed:

1) The depth to which chemical is initially found (L)

2) The chemical's diffusion coefficient in free air (D^A)

3) The volume fraction of air in the soil (θ_A)

4) The volume fraction of water in the soil (θ_w)

5) The dimensionless Henry's law constant (H)

6) The soil bulk density (ρ)

7) The soil organic carbon partition coefficient (K_{oc})

8) The organic fraction of the soil (f_{oc})

9) The depth of water applied to the soil surface (D_w)

In addition, biological and chemical transformation rate data for the chemical are needed from the literature.

7.2.2.3 Output Description--

This screening method is not intended to be an overall model that considers the interacting effects of transport and transformation mechanisms. Rough values for the half-life of diffusion and the depth of penetration of chemicals at or near the soil/air interface can be obtained from these methods. These values, along with transformation data from the literature can be used to determine which mechanisms are important for a particular chemical and the effect of varying the input parameters.

7.2.2.4 Resource Requirements--

Resource requirements are minimal. Access to a laboratory or computer is not needed.

7.2.2.5 Ease of Use--

The values of the input parameters are easily obtained or approximated, and the equations in Table 7-2 are easily solved.

7.2.2.6 Previous Applications--

The authors use their screening method to evaluate the dominant mechanisms affecting six pesticides. They state that the method applies to other organic chemicals as well.

7.2.2.7 Availability/Documentation--

The method is described in Bomberger et al. (1983).

7.2.3 The Baehr-Corapcioglu Model

Baehr and Corapcioglu (1987) present a one-dimensional numerical model of solute and vapor transport in the unsaturated zone. The model is a simplification of a general transport and fate model (Corapcioglu and Baehr, 1987) of an immiscible contaminant. The numerical model assumes that part of the unsaturated zone contains a hydrocarbon plume, present at residual levels and thus, immobile. Within the plume, four phases exist: immiscible, water, air and solid. Above and below the plume, the water and air phases fill the void space of the porous medium. A user-specified number of constituents are assumed to partition from the hydrocarbon under equilibrium conditions. The constituents are then transported in the water and air phases, eventually contaminating both the groundwater and the atmosphere. Biodegradation of the constituents is modeled and the role of oxygen availability in limiting microbial activity is incorporated into the model. Abiotic transformations are considered insignificant. Conservation of mass equations for each constituent and for oxygen are presented in Table 7-3. In addition to the assumptions stated above, a number of assumptions associated with the model are listed here.

It is assumed that:

1) A vertical one-dimensional model adequately describes the transport and fate of the constituents. Because the one-dimensional model does not consider lateral diffusion, it will tend to overestimate fluxes to the atmosphere and aquifer.

2) The air phase is at constant atmospheric pressure and is therefore immobile. Because the air phase is immobile, transport is by diffusion only. Under normal conditions, this assumption is adequate. If remedial action includes forced aeration to stimulate microbial growth, the assumption becomes invalid.

3) Oxygen is present only in the air and water phases.

4) The soil is homogeneous and isothermal. Neither of these assumed conditions is expected under actual field conditions, but are used to make the solution of the model tractable.

5) A constant averaged recharge rate is used. The combination of a constant recharge and a homogeneous soil results in uniform volumetric water contents.

TABLE 7-3. IMPORTANT EQUATIONS IN THE BAEHR/CORAPCIOGLU MODEL

1) The conservation of mass equation for a constituent of the immiscible pollutant in the unsaturated zone at time > 0

$$\frac{\partial}{\partial t}\left[G_k\theta_a + C_k\theta_w + S_k\rho_s + I_k\theta_i\right] + b_g \frac{\partial^2 G_k}{\partial z^2} + b_c \frac{\partial^2 C_k}{\partial z^2} + c_g \frac{\partial G_k}{\partial z} + c_c \frac{\partial C_k}{\partial z} = - R_{bio}{}^{k} \qquad (1)$$

where

$$b_g = - D_{ka}\theta_a\xi_a \qquad (2)$$

$$b_c = - (d_w\alpha_L + D_{kw}\theta_w\xi_w) \qquad (3)$$

$$C_g = - \left[D_{ka} \frac{\partial \theta_a}{\partial z} \xi_a + D_{ka}\theta_a \frac{\partial \xi_a}{\partial \theta_a} \frac{\partial \theta_a}{\partial z}\right] \qquad (4)$$

$$c_c = q_{wz} \qquad (5)$$

and where

C_k = concentration of the kth constituent in the water phase

G_k = concentration of the kth constituent in the air phase

I_k = concentration of the kth constituent in the oil phase

S_k = concentration of the kth constituent in the adsorbed phase

ρ_s = soil bulk density

θ_w = volumetric content for the water phase

θ_a = volumetric content for the air phase

θ_i = volumetric content for the oil phase

$R_{bio}{}^{k}$ = total microbial degradation rate

q_{wz} = vertical specific discharge for the water phase

$d_w\alpha_L$ = longitudinal mechanical dispersion coefficient for the water phase

$D_{kw}\theta_w\xi_w$ = effective soil diffusion constant for the water phase

$D_{ka}\theta_a\xi_a$ = effective soil diffusion constant for the air phase

k = number of the constituent

t = time

z = vertical distance

TABLE 7-3. IMPORTANT EQUATIONS IN THE BAEHR/CORAPCIOGLU MODEL (continued)

2) The boundary conditions associated with Equation (1)

$$G_k(z_{sur}, t) = 0 \qquad t > 0 \tag{6}$$

$$\left.\frac{\partial C_k}{\partial z}\right|_{(z_{wat}, t)} = 0 \qquad t > 0 \tag{7}$$

where

z_{sur} = the location of the soil surface

z_{wat} = the location of the water table

3) The initial conditions associated with Equation (1)

$$C_k(z,0) = 0 \qquad \{z_{hi} < z \le z_{sur}\} \text{ or } \{z_{wat} \le z < z_{low}\} \tag{8}$$

$$I_k(z,0) = I_{ko} \qquad z_{low} \le z \le z_{hi} \tag{9}$$

where

z_{hi} = the top of the immiscible plume

z_{low} = the bottom of the immiscible plume

4) The conservation of mass equation for free oxygen in the unsaturated zone for time > 0

$$\frac{\partial}{\partial t}\left[(H_{O_2}\theta_w + \theta_a)G_{O_2}\right] + b_g^* \frac{\partial^2 G_{O_2}}{\partial z^2} + b_c^* \frac{\partial^2}{\partial z^2}(H_{O_2}\, G_{O_2})$$

$$+ c_g^* \frac{\partial G_{O_2}}{\partial z} + c_c^* \frac{\partial}{\partial z}(H_{O_2}\, G_{O_2}) = -\sum_{k=1}^{N}(r_k\, R_{bio}^k) \tag{10}$$

where

$$b_g^* = -D_o^* \theta_a \xi_a \tag{11}$$

$$b_c^* = -(d_w \alpha_L + D_o \theta_w \xi_w) \tag{12}$$

$$c_g^* = -\left[D_o^* \frac{\partial \theta_a}{\partial z}\xi_a + D_o^* \theta_a \frac{\partial \xi_a}{\partial \theta_a}\frac{\partial \theta_a}{\partial z}\right] \tag{13}$$

$$c_c^* = q_{wz} \tag{14}$$

TABLE 7-3. IMPORTANT EQUATIONS IN THE BAEHR/CORAPCIOGLU MODEL (concluded)

and where

G_{O_2} = concentration of oxygen in the air phase
H_{O_2} = Henry's law constant for oxygen
r_k = stoichiometric factor relating the mass of oxygen required to degrade the kth constituent (3.5 for gasoline)
$D_o\theta_w\xi_w$ = soil diffusion constant for oxygen in water
$D_o^*\theta_a\xi_a$ = soil diffusion constant for oxygen in air

5) The boundary conditions associated with Equation (10)

$$G_{O_2}(z_{sur}, t) = (G_{O_2})_{atm} \qquad t > 0 \qquad (15)$$

$$\left.\frac{\partial G_{O_2}}{\partial z}\right|_{(z_{wat}, t)} = 0 \qquad t > 0 \qquad (16)$$

where

$(G_{O_2})_{atm}$ = atmospheric concentration of oxygen

6) The initial condition associated with Equation (10)

$$G_{O_2}(z, 0) = (G_{O_2})_{atm} \qquad z_{wat} \leq z \leq z_{sur} \qquad (17)$$

6) The soil/atmosphere and unsaturated/saturated interfaces are sharp boundaries. Therefore, the capillary fringe is not modeled. At the atmospheric boundary, the vapor concentration is assumed zero. The constituents cross the water table boundary by advective transport in the water phase only.

7) Biodegradation is aerobic. The microbial growth is affected only by the availability of a carbon source and oxygen. All other conditions (e.g. temperature and moisture content) are assumed to be at optimal levels. No acclimation period is needed for the microorganisms to begin consuming the constituents. Further, microbial growth does not affect the soil properties.

8) The rate of biodegradation is calculated by setting it equal to its stoichiometric equivalent of available oxygen. Thus, it represents an upper bound on microbial activity.

Using the numerical model to simulate a hypothetical gasoline with eight constituents, the authors observed that the fate of the constituents is very sensitive to the diffusive properties of the soil. When diffusion is not modeled, biodegradation rates are low because limited oxygen is available and the amount of constituents entering the ground water increases. Large diffusive air-phase fluxes result in volatilization of the constituents and decreased ground-water contamination. Biodegradation rate increases are not proportional to increased oxygen diffusion, however. The authors explain that conditions favorable to biodegradation are also favorable to volatilization. The constituents escape before they are biodegraded.

Because the model is very sensitive to the soils diffusive properties, such as the tortuosity factor, the authors state that field work to measure the diffusive properties is needed before this model is applied to a specific site.

The numerical solution to the equations in Table 7-3 is presented in an appendix to Baehr and Corapcioglu (1987). The output of the model provides an estimate of the amount of each constituent which enters the aquifer or which volatilizes into the atmosphere.

7.2.4 The Seasonal Soil Compartment Model (SESOIL)

SESOIL is a compartmental unsaturated zone environmental fate model, developed by Bonazountas and Wagner (1984) and updated by Hetrick et al. (1989) for the Environmental Protection Agency. The computer code, which uses both numerical and analytical techniques, was not run for the preparation of this report. Therefore, the brief summary presented below is based chiefly on the work of Watson and Brown (1984), who tested and evaluated the SESOIL model.

SESOIL consists of a compartmental moisture module and a compartmental solute transport module. Mass conservation equations are applied to representative soil layers over specified times. Estimates of pollution distribution after a season (e.g. a month or year) are based on the interaction of independent compartments (i.e. the air, water, and solid phases) within the soil.

The model assumes that each soil layer has uniform properties and that the gaseous, aqueous, and solid phases are in equilibrium. A free organic phase can not be modeled.

Volatilization is based on the steady-state diffusion of a chemical in the gaseous phase. The model assumes that the pollutant is buried under a clean layer of soil. Thus, vapor phase diffusion is rate controlling. Because the model allows for the redistribution of the water phase, steady-state diffusion may be an invalid assumption.

Adsorption is modeled as an equilibrium process and is assumed to be completely reversible. As was discussed in Section 7.2.2.1, both of these assumptions may tend to overestimate air emissions.

Degradation is modeled as a first-order decay process. Other transformation mechanisms, such as hydrolysis and cation exchange can also be modeled.

SESOIL can be used to evaluate the general behavior of a chemical applied to a subsurface environment. Thus it is a useful screening-level fate model. The input requirements are simple to moderate relative to more detailed models. The output consists of monthly summaries of the quantity of pollutant lost to each fate mechanism, as well as the percent leached to the ground water.

The performance of the model has been tested using six halogenated organics in hypothetical scenarios (Bonazountas and Wagner, 1984b). It has been applied to two landfarming sites, and has also been used by McLearn et al. (1988) to examine the environmental fate of hydrocarbon constituents.

SESOIL is in the public domain and can be obtained by contacting R.F. Kinerson, Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, DC.

7.2.5 The Risk of Unsaturated/Saturated Transport and Transformation Interactions for Chemical Concentrations Model (RUSTIC)

RUSTIC, a deterministic model, consists of three linked submodels which predict the fate of contaminants in the plant root zone, vadose zone, and saturated zone (Dean et al., 1989a; Dean et al., 1989b). The fate of either three unrelated chemicals or a parent chemical and up to two daughter products can be simultaneously modeled. The fate of non-aqueous fluid wastes can not be simulated. The submodels are linked by means of an execution supervisor, which allows the submodels to be run individually or in linked mode. RUSTIC also includes a Monte Carlo pre- and post-processor for use in performing exposure assessments. The following description of the RUSTIC submodels is taken from Dean et al. (1989a).

PRZM, the Pesticide Root Zone model (Carsel et al., 1984), is used as the root zone submodel in RUSTIC. It is a one-dimensional, dynamic, compartmental model. The root zone is treated as a series of soil layers which can vary in characteristics and thickness. Two major components--hydrology and chemical transport--are modeled. The hydrology component can consider runoff, erosion, evapotranspiration, irrigation, and water flow to the vadose or the saturated zone. The chemical component simulates pesticide uptake, first-order lumped decay, volatilization, advection, dispersion, and retardation. The effects of soil temperature variations and of a stagnant boundary layer above the soil surface on volatilization are included in PRZM. Chemical movement is a function of chemical properties, application rate, initial conditions, meteorological conditions, and soil characteristics.

VADOFT, the vadose zone submodel (Huyakorn et al., 1988a), is a Galerkin finite element code which simulates one-dimensional, single-phase moisture and solute transport in unconfined, variably saturated porous media. The fluid is assumed isothermal and homogeneous and hysteresis is assumed negligible. Linear equilibrium sorption, first-order decay, advection, and dispersion are modeled. VADOFT is used to predict infiltration and solute mass flux to the saturated zone.

SAFTMOD, the saturated zone submodel (Huyakorn et al., 1988b), is a finite element code which simulates two-dimensional flow and transport in either confined or unconfined aquifers. Areal, vertical, or axisymmetric simulations can be performed for single or for leaky two-aquifer systems. Both steady-state and transient runs can be made. When linked to PRZM and VADOFT, however, only transient simulations are allowed. Transport processes included in SAFTMOD include linear equilibrium sorption, first-order decay, advection, and hydrodynamic dispersion.

PRZM, the only submodel of RUSTIC which can be used to estimate air emissions, has been extensively tested and used as a stand-alone model. PRZM has been tested with pesticide application field data from sites in Florida, New York, Maryland, and Georgia with good results. It has also been used to study leachate migration from hazardous waste sites (Donigian and Bicknell, 1986). RUSTIC is currently being applied to test sites in Iowa, New York, and New Jersey.

RUSTIC is in the public domain and can be obtained by contacting R.F. Carsel, Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, GA.

7.2.6 Other Models of the Unsaturated Zone

Several models which consider the transport and fate of organic pollutants in the unsaturated zone are summarized in this section. Three papers include biodegradation as a first-order decay term, but do not consider the partitioning of a soluble pollutant into the vapor phase. Rather, a separate species, assumed to be a product of biotransformation, is modeled in the gas phase. Two other papers neglect chemical and biological transformation, altogether.

Angelakis and Rolston (1985) present a mathematical model which simulates the transformation of insoluble and soluble carbon species to carbon dioxide and the transport of all three species as a function of time and space. It is assumed that first-order biological kinetics are responsible for the transformations. The insoluble species is transported by convection. Convective-dispersive transport moves the soluble species, and the carbon dioxide is transported by diffusion. Adsorption/desorption of the first two species and a constant gas solubility are also accounted for in the model. Numerical simulation results compare favorably with laboratory data using soil columns and primary wastewater effluent.

Angelakis et al. (in press, 1989) develop an analytical solution to the one-dimensional gas diffusion equation coupled to a one-dimensional convective-dispersive equation for solute transport. First-order transformation from the soluble species to the gaseous species and linear, equilibrium adsorption of the soluble species are assumed. Results of the analytical solution compared reasonably with experimental data of the simultaneous transport of NO_3^- fertilizer and N_2O. The authors have extended their work to determine the analytical solution for transient gas diffusion coupled to two equations for convective-dispersive solute transport. This extension is explained in a paper currently under review for publication (Angelakis et al., in review, 1989).

Baehr (1987) develops a numerical solution for a system of partial differential equations defining radial transport of solutes and vapors which have partitioned from an immiscible multicomponent pollutant, such as oil. It is assumed the immiscible phase is immobile, that no chemical or biological transformations occur; that the soil is homogenous, isotropic, and isothermal, that the vapor migrates by means of diffusion only; and that equilibrium approximations describe the partitioning of the contaminant. Model results indicate that vapor and solute transport of constituents of an immiscible pollutant, present at residual levels, can cause contamination of the underlying ground water and the air.

In a two-part paper, Abriola and Pinder (1985) present a theoretical development and one-dimensional numerical solution of equations describing multi-phase transport of an organic pollutant. The simultaneous migration of a one- or two-component organic in three phases (immiscible, aqueous, and gaseous) can be simulated. Local equilibrium between the phases is assumed and convection of the vapor is neglected. No biological or chemical transformations are considered in the model. An example application of the model is presented by the authors.

7.3 SATURATED ZONE MODELS

7.3.1 The Swallow-Geschwend Model

Swallow and Geschwend (1983) present a mathematical model which can be used to predict the steady-state vertical flux of a volatile organic compound (VOC) from shallow aquifers. Equations describe vertical flux through three homogeneous regions of the subsurface: the saturated zone, the capillary fringe, and the unsaturated zone. The equations, which are shown in Table 7-4, are based on Fick's law and Henry's law.

Equation 1 assumes that flow in the aquifer is one-dimensional and horizontal. Vertical transport of the organic solute occurs only by means of vertical transverse dispersion. The VOC flux within the capillary fringe is the result of both vertical dispersion in the liquid phase and diffusion in the gaseous

TABLE 7-4. IMPORTANT EQUATIONS IN THE SWALLOW/GESCHWEND MODEL

1) Volatile organic carbon (VOC) flux in the saturated zone

$$\text{Saturated Flux} = a_t \bar{v} \frac{dC_w}{dz} \tag{1}$$

where

a_t = vertical transverse dispersivity (cm)
$\bar{v}$ = linear flow velocity (cm/day)
C_w = VOC concentration in the pore water (mass/cm^3 water)
z = depth from the bottom of the aquifer to the capillary fringe (cm)

2) VOC flux in the capillary fringe.

$$\text{Capillary Fringe Flux} = \left[a_t \bar{v} \frac{(w(z) - w_o)^3}{(n - w_o)^3} + \frac{HD^*(n - w(z))}{t} \right] \frac{dC_w}{dz} \tag{2}$$

where

$w(z)$ = water content
w_o = irreducible water content
n = porosity
H = dimensionless Henry's law constant
D^* = molecular diffusion coefficient of the VOC in free air (cm^2/day)
t = tortuosity factor

3) VOC flux in the unsaturated zone

$$\text{Unsaturated Flux} = D^* (n - w_o) \frac{dC_a}{dz} \tag{3}$$

where

C_a = VOC concentration in the pore air (mass/cm^3 air)
z = depth from the capillary fringe to the ground surface (cm)

phase. Partitioning between the liquid and gaseous phases is assumed to be rapid. Henry's law is applied to describe equilibrium partitioning between the two phases. Within the unsaturated zone, only diffusion of the VOC in the gaseous phase is considered.

The model does not incorporate the retarding affects of adsorption or of chemical and biological transformations. Therefore it will tend to overpredict the emission of VOCs from the subsurface. Another limitation of the model is the assumption of homogeneous conditions. The authors point out that in a heterogeneous soil environment, the rate of flux will be limited by the most retarding layer.

The affect of the vertical transverse dispersivity value, a_t, on the flux is discussed. Dispersivity is proportional to the scale over which it is measured. For small values of a_t, the flux is limited by transport in the saturated zone and thus, is small. Conversely, for large values of a_t, the flux in the unsaturated zone is limiting. Model predictions suggest that vertical transport of VOCs from shallow aquifers may become significant for values of a_t between 1 and 10 cm. Some laboratory work and preliminary field work by the authors suggests that volatilization from contaminated aquifers can occur, but they also state that much more work is needed before its importance is known.

7.3.2 Saturated Zone Models Which Consider Biodegradation

In recent years, several models have been developed to simulate transport and biodegradation in the saturated zone. Because the models can not be used to predict air emissions directly, only brief summaries are presented. They could be used in conjunction with unsaturated zone models to estimate the emission of pollutants from the subsurface to the atmosphere.

One biofilm model and six dispersed-growth models are introduced. In general, dispersed-growth models have a simpler mathematical construction, which allows two-dimensional codes to be written. None of the dispersed-growth models deals with secondary utilization of trace organics. Either a primary organic substrate or an electron acceptor are rate-limiting.

Rittmann et al. (1980) present a method which can predict biotransformations of trace organics in the area near an injection well, where biofilm growth can occur. First, a steady-state biofilm model and a one-dimensional solute transport code are combined to predict both removal of a primary substrate and biofilm thickness. The biofilm thickness is then coupled with known concentrations and parameters for a secondary substrate of interest in a non-steady-state biofilm model.

A model by Sykes et al. (1982) predicts the concentration of landfill leachate, measured as COD, in ground water. A one- or two- dimensional Galerkin finite element code is used to determine the transport and anaerobic degradation of a leachate plume. Methane fermentation of volatile fatty acids is assumed to be the rate-limiting process. Michaelis-Menton kinetics are used to simulate substrate utilization and microbial growth on high substrate concentrations. When substrate concentration is much less than the half saturation constant, first-order kinetics are applied. Adsorption of the leachate is assumed negligible, as is the movement of microorganisms. The model predicts that substantial biodegradation occurs within a short distance of a landfill.

Corapcioglu and Haridas (1985) consider the possible modes of transport and attenuation of bacteria and viruses introduced into an aquifer. One- and two-dimensional Galerkin finite element methods are used to model the fate of microorganisms in the presence of a primary substrate. Straining, sedimentation in pores, and adsorption are the chief removal mechanisms for bacteria. Periodic sloughing counterbalances the clogging mechanisms. The authors incorporate these mechanisms into their model as a rate-controlled process for bacteria. A first-order decay rate and Monod growth equation are also included.

Molz et al. (1986) present a one-dimensional numerical model of substrate and oxygen transport in an aquifer. Aerobic biodegradation, which is described by Monod kinetics, can be limited by either oxygen or substrate availability. The microorganisms are assumed to grow in colonies of average thickness and radius, attached to the solid soil matrix. Transport into the biomass is limited by diffusion through a stagnant layer adjacent to the microbial colonies. The model equations are solved using a Eulerian-Lagrangian finite-element scheme.

A one- or two-dimensional model, developed by Borden and Bedient (1986) and later applied to a shallow aquifer contaminated by hydrocarbons (Borden et al., 1986), models oxygen transport and consumption as well as the movement and fate of a primary substrate. Monod kinetics are modified so that microbial growth, as well as oxygen and hydrocarbon removal rates, are dependent on both hydrocarbon and oxygen concentrations. Adsorption and microbial movement are simulated using retardation factors, which assume the processes are linear and instantaneous.

Simulations performed by the authors show that three zones develop down-gradient from a source of contamination. Close to the source, microbial mass increases significantly and oxygen is almost completely depleted. Within the dissolved contaminant plume, mass transfer of oxygen is rate-limiting. In front of the plume, the trace amounts of substrate or of naturally-occurring carbon sources may limit microbial growth. Sensitivity analyses indicate that substrate and oxygen utilization within the contaminant plume can be approximated as instantaneous reactions. This means simulation of microbial concentration is no longer required, simplifying the numerical solution.

Widdowson et al. (1988) present a one-dimensional model of biodegradation by facultative microorganisms in the saturated zone. The model, which is similar in structure to that of Molz et al. (1986), considers both oxygen- and nitrate-based respiration. Equations for the transport of a primary substrate, dissolved oxygen and nitrate, and ammonia nitrogen, any of which can limit microbial growth, are developed. An equation for the growth and decay of microorganisms, which are attached to the soil matrix, is also developed. An example application of the model for a hypothetical experiment using data from the literature is presented.

Rifai et al. (1988) extend the modeling work of Borden et al. (1986) to produce a two-dimensional model of the transport and biodegradation of hydrocarbons and the transport of oxygen. The authors have modified the U.S. Geological Survey Method of Characteristics model (Konikow and Bredehoeft, 1979) to utilize an dual-particle-mover concept. The model, which assumes instantaneous substrate and oxygen utilization, was applied successfully to an aviation fuel spill site.

Kindred and Celia (1989) extend the techniques of Molz et al. (1986) and Borden and Bedient (1986) to present mathematical conceptualizations of biodegradation in aquifers. Both aerobic and anaerobic degradation are included in a contaminant transport model. In addition, the authors consider the uptake of multiple organic substrates, cometabolism, the effect of inhibitory substrates, and diffusion through the biomass. The model, which is in the form of coupled non-linear reactive transport equations, further coupled to growth equations, is solved using a new numerical technique, called the optimal test function method.

SECTION 8

MODELS OF RELATED PHYSICAL REMEDIATION PROCESSES

8.1 INTRODUCTION

Two relatively new non-biological treatment processes are included in this report because each of the two processes can be used in conjunction with bioremedial efforts. Because the processes are new, they are largely undemonstrated techniques and published research is limited.

Soil venting is an in-situ technique for removing volatile organic vapors from the unsaturated zone. Using vacuum pumps, and possibly air injection pumps also, an air flow field is established in the soil. The extraction of contaminant vapors by the vacuum pump causes adsorbed and liquid-phase organics in the soil to volatilize. Although the physical extraction of vapors dominates all other processes, the establishment of an air flow field simultaneously stimulates microbial activity by providing a plentiful supply of oxygen.

Soil washing is a technique used to reduce the volume of contaminated soil at a site which needs to be treated. Thus it is only one component in an overall treatment process, which often includes a bioremedial component as well. In the soil washing process, excavated soils are physically scrubbed and screened to separate the fines and larger particles. The larger sands and gravels are usually cleaned sufficiently by the scrubbing, while the separated fine soil particles, to which organic pollutants tend to adsorb, need further treatment. The water in which the soil is agitated also needs further treatment. Any of a number of suspended-growth or fixed-film bioremedial processes can be used to treat the contaminated water, depending on site-specific conditions.

The state-of-the-art in modeling these two physical processes is briefly described below.

8.2 SOIL VENTING MODELS

Most unsaturated zone models assume the air phase is immobile. Two papers in the literature discuss the modeling of air flow in the unsaturated zone. The air-flow models can aid in the design of soil venting systems, but reveal nothing about vapor transport and emissions. Baehr et al. (in press 1989) present a mathematical model of radially-symmetric air flow. By calibrating the model with pressure data from pumping tests, the air permeability of the unsaturated zone, and the spacing and screen intervals of pumping wells can be evaluated. A successful application of the model to a contaminated field site is described by the authors. Massmann (1989) describes techniques which can be used to apply ground-water flow models to soil venting system design. If the maximum pressure difference between any two points in the flow field is less than approximately 0.5 atmospheres, which is generally the case at soil venting sites, the author explains that ground-water flow equations provide a good approximation to air flow, given the properly defined set of parameters. The author illustrates the methodology using data from a field site.

Only one paper discusses advective vapor transport. Baehr et al. (in press 1989) present a one-dimensional model of vapor transport under high air flow conditions and in the presence of an immiscible phase. The model was developed by generalizing an unsaturated zone model (Baehr and Corapcioglu, 1987), described in Section 7.2.3, to include advective air-phase transport and then making a number of simplifying assumptions. The model was used to predict transport during laboratory column experiments.

An unreleased finite-element model of compressible air flow in the subsurface (FEMAIR) has been developed by Yeh et al. An article and user's guide, which describe the model, are currently being prepared. According to the authors, the code can be used to predict air emissions of volatile organics from the soil venting process (Yeh, personal communication). The code is undergoing review and is not available at present. When released, it will be in the public domain.

8.3 SOIL WASHING MODELS

Extensive conversations with experts researching the soil washing process have led to the conclusion that no soil washing models which include kinetics exist. The only modeling work identified was done by the EPA to determine the volume of soil that can be treated.

Uncovered soil washing tanks can be a significant source of volatile organic air emissions, but the emissions are difficult to estimate. The ratio of soil-to-water during the scrubbing process can vary. In some applications, a slurry mixture is used, in others, a froth floatation method, involving much more water and diffused aeration, is employed. Research into air emissions from this process is needed before realistic models can be developed. Field studies of air emissions from a soil washing apparatus, sponsored by the EPA are planned for this year.

SECTION 9

RESEARCH NEEDS

9.1 INTRODUCTION

In recent years, the emission of volatile organics from biological treatment facilities has become an issue of concern. In order to estimate the magnitude of emissions from these facilities, overall fate models which incorporate the effects of several competing removal mechanisms are needed. While such models have been developed for some bioremedial processes, no models exist for other processes. The models which are available are of limited utility both because of limited laboratory and field data and because of the assumptions made in developing the models. The need for further research and data collection, which exists on several fronts, is discussed below in terms of 1) the removal mechanism kinetics, 2) the limitations of the current models, and 3) the need for a framework to evaluate emissions from new bioremediation processes.

9.2 REMOVAL MECHANISM KINETICS

Accurate prediction of the environmental fate of a chemical requires an understanding of the kinetics of the mechanisms affecting its removal. Most kinetic research has focused on laboratory studies of single chemicals. It is questionable whether results obtained from laboratory experiments are directly applicable to field sites, where multiple waste components interact with a heterogeneous environment. The validity of applying kinetic models developed from small-scale laboratory research to full-scale facilities needs to be confirmed through more extensive field studies. The field studies should further investigate the accuracy of treating kinetic processes as independent and simultaneous reactions.

Several well-known equilibrium models of the adsorption process are available and are widely used by modelers. Linear equilibrium isotherms are most commonly used. Correlations have been developed which make it possible to estimate the adsorption coefficient from available data, but the applicability of those correlations needs further testing. Also the assumption that adsorption can be described by equilibrium relationships needs further investigation, particularly for the powdered activated carbon treatment process. Finally, the question of whether the concentration of solids affects partitioning in wastewater needs to be resolved. It is now commonly assumed that the adsorption partition coefficient is independent of solids concentration, but some evidence contradicts this assumption and the issue needs to be clarified.

The mass transfer of volatile organics to the air has been studied extensively and the correlations developed to estimate the mass transfer coefficient have been tested in the field to some extent (U.S. EPA, 1987b). Although more extensive field testing of the correlations is needed, the passive volatilization and stripping kinetic models can be used with some confidence.

On the other hand, most researchers agree that the biodegradation of organics in biological treatment facilities is poorly understood. A number of biokinetic models have been proposed to fit biodegradation rate data. The most common are Monod and first-order expressions, but there is no general agreement about which models are most appropriate. Several problem areas, which have prevented a good understanding of biodegradation at field sites, are discussed here.

1) It is likely that only a small number of the microbial species present in a treatment facility degrade a particular compound. Because it is not possible at present to determine the fraction of the active biomass which degrades a compound, modelers usually assume the total active biomass is responsible for the degradation.

2) At many waste water treatment plants, a wide variety of hazardous chemicals may be present at concentrations too low to support growth. They are biodegraded as a secondary substrate. The effect of alternative substrates on the biodegradation rate of a particular compound in a multi-component waste needs greater attention, as does the interaction of primary and secondary substrates. Much of the kinetic data currently available in the literature for volatile organics is based on laboratory studies of single compounds at concentrations much higher than they are commonly found at treatment sites. This could account for the wide discrepancies which are observed between kinetic data from the laboratory and the field.

3) Cadena et al. (1989) point out other factors which make the transfer of laboratory data to field application difficult. Some laboratory studies have not accounted for volatilization and other loss mechanisms, but rather have assigned the total compound disappearance to biodegradation. Furthermore, the temperature, biomass concentration, and the volumetric water content in soils, which can all vary considerably between the laboratory and the field, have all been shown to affect results. Further research is needed to quantify biodegradation kinetics for hazardous compounds under a wide range of conditions, both aerobic and anaerobic.

4) Biodegradation rate constants are difficult and expensive to determine. In addition, because the rate constants are derived for a wide variety of kinetic expressions and conditions, published data must be used with caution. A user must determine that published data are appropriate for the model being used. Therefore, methods of estimating the constants from more readily available physical and chemical information or from simple tests are needed.

9.3 LIMITATIONS OF THE CURRENT MODELS

An ideal biodegradation model would allow the coupling of physical, chemical and biological processes. It would include multiple carbon donors and electron acceptors, a heterogeneous population and a heterogeneous growth medium in non-steady-state conditions. The effects of temperature, pH, and inorganic nutrients would be known. Finally, acclimation and inhibition of microorganisms exposed to new substrates would be quantified by kinetic formulations and accurate kinetic parameters would be known.

The models developed thus far have, out of necessity, made many simplifying assumptions about the processes affecting the fate of pollutants in the subsurface. Limits in both understanding and computational abilities have resulted in models best used for screening-level purposes (i.e., the model results are generally accurate within an order-of-magnitude only). As our understanding and skills increase, the models are also increasing in complexity.

A major limitation for most of the wastewater treatment models discussed in this report, when used to simulate specific sites, is the assumption of steady-state. Berglund and Whipple (1987) report that the daily average concentration of chemicals in wastewater varied by two to three orders-of-magnitude during a field study. They point out that the wide and rapid variation in waste loading at treatment facilities makes it difficult to relate air emission measurements taken over a short time period to the average values predicted by steady-state models. Because steady-state models do not represent actual field conditions and can not be used to predict changes in system capacity or in the quantity and quality of waste over time, it is difficult to verify their accuracy based on field data. Steady-state models have the advantage of simplicity and have value at the present time for screening purposes. As the availability of data and the understanding of biodegradation kinetics increases, it will be necessary to give more attention to the development of dynamic models.

The use of homogeneous and constant properties to describe conditions at a site is another common simplifying assumption which should be reexamined. This is particularly true at land treatment or in-situ sites, where soil properties can vary widely.

As mentioned above, the majority of the models described in this report are best used to screen the expected fate of specific chemicals in the environment or to construct a range of scenarios for a particular bioremediation process. Modeling results have been shown to be sensitive to all the biological parameters (U.S. EPA, 1987b), for which data are currently sparse and unreliable. Unless accurate biological data are available for a modeling study, the use of worst-case scenarios, in which biodegradation is assumed to be negligible, should be included in any screening study.

Fixed-film bioremedial processes are not as well understood as suspended growth systems. In addition, the physical complexity of fixed-film treatment facilities makes them difficult to model. A number of models have been published that simulate reactions within a fixed biofilm. A few models go further to incorporate system hydraulics and mass transfer of electron acceptors, such as oxygen. No published models specifically address the issue of air emissions from fixed-film processes. The development of such models, and at the same time, the collection of laboratory and field data on air emissions is needed.

Most of the models in this report focus on aerobic processes. The extent of air emissions from anaerobic processes treating hazardous waste has not been addressed in the literature yet. Volatile organics can escape with the gases produced during anaerobic biodegradation. Research into this subject should not be neglected.

The application of several of the bioremediation processes described in this report (e.g., composting) to treat hazardous waste is still in the early stages of research. If researchers keep the issue of air emissions in mind as they design experiments to investigate these processes, the development of a useful data base will be expedited.

9.4 EVALUATING EMISSIONS FROM NEW BIOLOGICAL TREATMENT PROCESSES

New chemicals are produced every year, and over time, new bioremediation processes emerge. A framework is needed to evaluate the likelihood of air emissions both of new chemicals and from new processes. A valuable tool would be a comprehensive data base which identifies and groups chemicals based on their expected fate in current treatment facilities (Jury, 1983). The expected fate of new chemicals could be determined based on the behavior of existing chemicals with similar characteristics. The data base could also be used to predict emissions from treatment processes with design characteristics similar to existing bioremediation processes.

SECTION 10

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